



(19) Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) EP 0 413 482 B1

(12) EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention  
of the grant of the patent:  
12.03.1997 Bulletin 1997/11

(51) Int Cl.<sup>6</sup>: H01J 43/24, H01J 9/12

(21) Application number: 90308571.0

(22) Date of filing: 03.08.1990

(54) Thin-film continuous dynodes

Kontinuierliche Dünnschicht-Dynoden  
Dynodes continus du type à couche mince

(84) Designated Contracting States:  
DE FR GB NL

(30) Priority: 18.08.1989 US 395588

(43) Date of publication of application:  
20.02.1991 Bulletin 1991/08

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(56) References cited:  
EP-A- 0 066 926 EP-A- 0 215 699  
FR-A- 2 220 487 GB-A- 2 040 553  
US-A- 4 780 395

- JOURNAL OF PHYSICS E: SCIENTIFIC INSTRUMENTS, vol. 12, no. 11, 1979, pages 1015-1022, GB; L.P. ANDERSSON et al.: "The parallel-plate electron multiplier"

EP 0 413 482 B1

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**Description**

The invention relates to channel electron multipliers and microchannel plates.

5 Channel electron multipliers 10 (CEMs) (Fig. 1) and microchannel plates 20 (MCPs) (Fig. 2) are efficient, low-noise, vacuum-electron amplifiers with typical gains ( $G = I_o/I_i$ ) in the range of  $10^3 - 10^8$  where  $I_o/I_i$  is the ratio of the output to input currents. CEMs 10 are devices which have a single channel 12 and are generally used for direct detection of charged particles (e.g., electrons and ions) and photons from soft X-ray to extreme ultraviolet wavelengths (i.e., 1 - 100 nm). They are mainly used as detectors in a wide variety of scientific instrumentation for mass spectrometry, electron spectroscopy for surface analysis, electron microscopy, and vacuum ultraviolet and X-ray spectroscopy.

10 MCPs 20 are fabricated as areal arrays of millions of essentially independent channel electron multipliers 22 which operate simultaneously and in parallel. Using an MCP, direct detection of charged particles and sufficiently energetic electromagnetic radiation can be achieved in two dimensions over large areas (up to several hundred  $\text{cm}^2$ ), with good resolution (channel spacing or pitch < 10  $\mu\text{m}$ ), at fast response times (output pulse widths < 300 ps), and with linear response over a broad range of input event levels ( $10^{-12}-10^{-8}\text{A}$ ). By placing an MCP between a suitable photocathode 15 and fluorescent screen in an optical image tube (not shown), two-dimensional signals from the ultraviolet to the near-infrared spectral region can be intensified and displayed as a visible image. While MCPs continue to find major application in image tubes for military night-vision systems, there is now growing interest in MCPs for high-performance commercial applications as well. These presently include high-speed and high-resolution cameras, high-brightness displays, and state-of-the-art detectors for scientific instrumentation.

20 CEMs and MCPs essentially consist of hollow, usually cylindrical channels. When operated at pressures  $\leq 1.3 \times 10^{-4}$  Pa ( $10^{-6}$  torr) and biased by an external power supply, such channels support the generation of large electron avalanches in response to a suitable input signal. The cutaway view of Fig. 1 shows CEM 10 in operation. The process of electron multiplication in a straight channel does not critically depend on either the absolute diameter ( $D$ ) or length ( $L$ ) of the channel, but rather on the  $L/D$  ratio ( $\alpha$ ). For a curved channel, the ratio ( $\beta$ ) of the channel length  $L$  to the 25 radius of channel curvature ( $S$ ),  $L/S$ , is the important parameter. These geometric ratios largely determine the number of multiplication events ( $n$ ) that contribute to the electron avalanche. Typical values of  $\alpha$  range from 30 to 80 for conventional CEMs and MCPs with channel diameters  $D$  on the scale of 1 mm and 10  $\mu\text{m}$ , respectively. Thus, a CEM 10 is a single channel electron multiplier of macroscopic dimensions while MCP 20 is a wafer-thin array of microscopic electron multipliers with channel densities of  $10^5-10^7/\text{cm}^2$ .

30 The channel wall 14 of CEM 10 or the wall 24 of the MCP 20 acts as a continuous dynode for electron multiplication and may be contrasted with the operation of photoemissive detectors using discrete dynodes (e.g., an ordinary photomultiplier tube). In operation, the continuous dynodes 14 and 24 must be sufficiently resistive to support a biasing electric field ( $\epsilon$ ) =  $10^2-10^5$  V/cm without drawing an excessive current. They must also be conductive enough such that a discharging current is available to replenish electrons emitted from the dynode 14,24 during an electron avalanche.

35 For example, when a signal event 30 such as an electrically charged particle (Fig. 1) (e.g., an electron or a  $\text{Ne}^+$  ion) or sufficiently energetic radiation (e.g., an X-ray photon) strikes the channel wall 14 near the negatively biased input end 32, there is a good probability that electrons 34 will be ejected from the surface 14. These primary electrons 34 are accelerated down the channel 12 by an applied electric field  $\epsilon$  (see arrow 36) produced by the bias potential ( $V_B$ ) represented by the power supply 38.  $\epsilon = V_B/L$ , where  $V_B$  in volts  $\sim 20-25\alpha$  for a conventional straight-channel multiplier.

40 Collision of the emitted electrons 34 with the channel wall 14 causes the emission of secondary electrons 40. These secondary electrons in turn act as primary electrons in subsequent collisions with the channel wall 14 which produce another generation of secondary electrons. Provided that more than one secondary electron is emitted for every incident primary electron, the secondary electron yield ( $\delta$ )  $> 1$ , and  $n$  repetitions of this primary collision-secondary emission sequence in the direction of the output end 41 rapidly leads to an output electron avalanche 42 of magnitude  $\delta^n$ .

45 The near-surface region of the dynode 14 must have an average value of  $\delta$  sufficiently greater than unity to support efficient multiplication of primary electrons impinging on a channel wall with energies ( $E_p$ ) mostly in the range of 20-100 eV. For materials with good secondary electron emission properties,  $\delta$  initially increases with  $E_p$  from  $\delta < 1$  to  $\delta = 1$  at the first crossover energy  $E_p^1$ , and then to  $\delta > 1$ . Emissive materials of greatest interest for electron multipliers tend to have values of  $E_p^1$  in the range of about 10 eV  $\leq E_p^1 \leq 50$  eV, the smaller the better. For such materials, a linear approximation of  $\delta(E_p)$  is  $\delta = E_p/E_p^1$  for  $E_p \leq 100$  eV. As an example, if  $E_p^1 = 30$  eV for the continuous dynodes in conventional CEMs and MCPs, then an estimate of the range of  $\delta$  for primary electrons with  $E_p = 20-100$  eV is  $0.7 \leq \delta \leq 3.3$ . Now, for a straight-channel multiplier with  $\alpha = 40$ ,  $V_B = 1000$  V,  $E_p^1 = 30$  eV, and a most probable initial energy ( $E_s$ ) = 3 eV for a secondary electron as it emerges from the dynode surface, the electron gain  $G$  from a single input electron is approximately calculated as follows:

5

$$G = \delta^n = \left[ \frac{E_p}{E_p^I} \right]^n$$

10

$$= \left[ \frac{(qV_B)^2}{(4E_s E_p^I \alpha^2)} \right] \sqrt{\frac{4E_s^2}{qV_B}}$$

15

$$= 4 \times 10^4.$$

The most probable collision energy of the primary electrons

20

$$(\bar{E}_p) = (qV_B)^2 / 4E_s \alpha^2 \approx 52 \text{ eV};$$

the average yield or gain per multiplication event

25

$$\delta = (qV_B)^2 / 4E_s E_p \alpha^2 \approx 1.75;$$

the number of the multiplication events

30

$$n = 4E_s \alpha^2 / qV_B \approx 19; \text{ and,}$$

$q$  is the magnitude of electronic charge.

When the electron avalanche emerges from the channel as an output signal, it typically represents a very large amplification of the original input signal. Because electron multiplication increases geometrically down the length of a channel, signal gains  $G$  ranging from  $10^3$  to  $10^8$  can be obtained depending upon the specific dynode materials, channel geometry, detector configuration, and application.

Straight-channel multipliers are limited to electron gains of about  $10^4$  due to a phenomenon known as positive ion feedback. Near the output end of a channel multiplier and above some threshold gain, residual gas molecules within the channel or gasses adsorbed on the channel wall can become ionized by interaction with the electron avalanche. In contrast to the direction of travel for electrons with negative electrical charge, positive ions are accelerated toward the negatively-biased input end of the channel. Upon striking the channel wall, these ions cause the emission of electrons which are then multiplied geometrically by the process described above. Spurious and at times regenerative output pulses associated with ion feedback can thus severely degrade the signal-to-noise characteristics of the detector.

An effective method for reducing ion feedback in channel multipliers is to curve the channel. Channel curvature restricts the distance that a positive ion can migrate toward the input end of a channel, and hence greatly reduces the amplitude of spurious output pulses. Single MCPs with straight channels typically provide electron gains of  $10^3$ - $10^4$ . Curved-channel MCPs can produce gains of  $10^5$ - $10^6$  but are difficult and expensive to manufacture. Curved-channel CEMs can operate at gains in excess of  $10^8$ .

MCPs 20 are usually fabricated with channels 22 that are inclined at an angle of  $\sim 10^\circ$  relative to a normal projection from the flat parallel surfaces 26 of the device. This is done to improve the first strike efficiency of an input event. Stacking MCPs and alternating the rotational phase of the channel orientation by  $180^\circ$  provides another means for overcoming ion feedback in MCP detectors. Two-stage (Chevron™) and three-stage (Z-stack) assemblies of MCPs thereby produce gains of  $10^6$ - $10^7$  and  $10^7$ - $10^8$ , respectively.

The channel wall of a CEM or MCP acts as a continuous dynode for electron multiplication and may be contrasted elsewhere with the operation of detectors using discrete dynodes (e.g., an ordinary photomultiplier tube). A continuous dynode must be sufficiently conductive to replenish electrons which are emitted from its surface during an electron avalanche. In analog operation of CEMs and MCPs at a given gain  $G$ , the output current  $I_o$  from a channel is linearly

related to the input current  $I_i$ ; providing the output does not exceed about 10% of the bias current ( $i_B$ ), imposed by  $V_B$ , in the channel wall. Above a threshold input level,  $I_i \sim 0.1 i_B/G$ , gain saturation occurs and current transfer characteristics are no longer linear. On the other hand, the continuous dynode must also be resistive enough to support a biasing field  $\epsilon = 10^2\text{-}10^5 \text{ V/cm}$  without drawing an excessive  $i_B$ , as manifest by thermal instability that is associated with Joule heating. Moreover, the near-surface region of the dynode must have an average value of  $\delta$  sufficiently greater than unity to support efficient multiplication of electrons impinging on a channel wall, as discussed above.

The electrical and electron emissive properties of continuous dynodes in the current generation of CEMs and MCPs critically depend on details of their manufacture. MCPs are presently fabricated by a glass multifibre draw (GMD) process that includes drawing a rod-in-tube glass fibre of a barium borosilicate core glass clad with a lead silicate glass; stacking the composite fibre into a hexagonal array and redrawing glass multifibre bundles; stacking of multifibre bundles and consolidating into a billet consisting of an array of solid core glass channels imbedded in a cladding glass matrix; wafering of the billet and surface finishing; wet chemical processing to remove the core glass leaving behind an array of hollow channels extending through a wafer of cladding glass; additional wet chemical processing to enhance secondary emission from the channel surface; reducing the lead silicate glass in a hydrogen atmosphere to render the dynode surface electronically conductive with a sheet resistance ( $R_s$ ) =  $10^{11}\text{-}10^{14} \Omega/\text{sq}$ ; and electroding of the flat surfaces of the MCP wafer.

Fabrication of CEMs is simpler; it entails thermal working of lead silicate glass tubing into a suitable geometry; reducing the glass in hydrogen to produce a continuous dynode surface with  $R_s = 10^6\text{-}10^8 \Omega/\text{sq}$ , and electroding. On account of the vastly different values of  $R_s$  that are required for continuous dynodes in MCPs versus CEMs, compositionally distinct lead silicate glasses have been formulated for each application.

The hydrogen reduction step is essential to the operation of conventional electron multipliers. Lead cations in the near-surface region of the continuous glass dynode are chemically reduced in a hydrogen atmosphere at temperatures of about  $350^\circ\text{-}500^\circ\text{C}$  from the  $\text{Pb}^{2+}$  state to lower oxidation states with the evolution of  $\text{H}_2\text{O}$  as a reaction product. The development of significant electronic conductivity in a region no more than about  $1 \mu\text{m}$  beneath the surface of reduced lead silicate glass (RLSG) dynodes has been explained in two rather different ways. One theory holds that a small fraction (i.e.,  $\sim 10^{-6}$ ) of the lead atoms within the reaction zone remains atomically dispersed in lower valence states (i.e.,  $\text{Pb}^{1+}$  and  $\text{Pb}^0$ ). An electron hopping mechanism via localized electronic states in the band gap, associated with lead atoms in the lower valence states, is said to give rise to electronic conduction. Another theory, noting that most of the lead atoms within the reaction zone are reduced to the metallic state and are agglomerated into droplet-like particles with a discontinuous morphology, suggests that electronic conduction derives from a tunnelling mechanism between such particles. Regardless of the mechanism that ultimately proves correct, one can expect that the electrical characteristics of RLSG dynodes are a complex function of the chemical and thermal history of the glass surface as determined by the details of its manufacture.

During hydrogen reduction, other high-temperature processes including diffusion and evaporation of mobile chemical species in the lead silicate glass (e.g., alkali, alkaline earth, and lead atoms) also act to modify the chemistry and structure of RLSG dynodes. Compositional profiles through the near-surface region of glasses that are used in the manufacture of MCPs have indicated that RLSG dynodes have a two-layer structure.

An exemplary RLSG dynode 50, shown in Fig. 3, comprises a superficial silica-rich and alkali-rich, but lead-poor dielectric emissive layer 52 about 2-20 nm in thickness (d) that produces adequate secondary emission (i.e.,  $E_p \sim 30 \text{ eV}$ ) to achieve useful electron multiplication. Beneath this dielectric emissive layer 52 (or dynode surface), a semiconductive lead-rich layer 54 about 100-1000 nm in thickness (t) serves as an electronically conductive path for discharging the emissive layer 52. Upon consideration of the ranges of  $R_s$  for RLSG dynodes given above and assuming the semiconductive layer 54 has a thickness  $t = 100 \text{ nm}$ , it can be readily shown that the bulk electrical resistivity ( $r$ ) of the material comprising semiconductive layer 54 is  $r = R_s \cdot t = 10^1\text{-}10^3 \Omega \cdot \text{cm}$  for CEM dynodes and  $r = 10^6\text{-}10^9 \Omega \cdot \text{cm}$  for MCP dynodes. A base glass 56 provides mechanical support for the continuous RLSG dynode 50 in the geometry of macroscopic channels for CEMs or arrays of microscopic channels for MCPs. The interface 58 shown schematically in Fig. 3 between the conductive 54 and emissive 52 layers in actual RLSG dynodes is rather less distinct than illustrated in Fig. 3; this schematic structure, however, does provide a useful model.

While the manufacturing technology of RLSG MCPs and CEMs is mature, relatively inexpensive, and reasonably efficient, it imposes important limitations on current device technology and its future development. These limitations are summarized as follows. Both electrical and electron emissive properties of RLSG dynodes are quite sensitive to the chemical and thermal history of the glass surface comprising the dynode. Therefore, reproducible performance characteristics for RLSG MCPs and CEMs critically depend upon stringent control over complex, time-consuming, and labour-intensive manufacturing operations. In addition, the ability to enhance or tailor the characteristics of RLSG MCPs and CEMs is constrained by the limited choices of materials which are compatible with the present manufacturing technology. Gain stability, maximum operating temperature, background noise, and heat dissipation in high-current devices are several key areas where performance is adversely affected by material limitations of the lead silicate glasses that are used in the manufacture of conventional MCPs and CEMs.

The GMD process also imposes important manufacturing constraints on the geometry, and hence on the performance and applications of RLSG MCPs in the following ways: channel diameters  $\geq 4 \mu\text{m}$  and channel pitches  $\geq 6\mu\text{m}$  in current practice limit temporal and spatial resolution; quasi-periodic arrays of channels within multifibre regions and gross discontinuities at adjacent multifibre boundaries greatly complicate the task of addressing or reading out individual 5 or small blocks of channels; variations in channel diameter from area to area in an array are manifest as patterns with differential gain; and the largest size of a microchannel array is now limited to a linear dimension on the order of 10 cm. Our copending application 90302243.2 (EP-A-0 386 955) addresses these problems.

Finally, despite the major market for MCPs in military night vision devices, other substantial applications for these remarkable detectors have been slow to evolve in part because they are difficult to interface with solid-state electronics. 10 Greater compatibility with semiconductor electronics (e.g., with regard to materials of construction, interconnection, or power requirements for operation) would facilitate the implementation of important new applications including commercial night vision, optical computing, and high-performance display, photographic, and imaging technologies.

US-A-4 780 395 teaches forming a secondary-emission, copper surface on the inner surfaces of a microchannel plate by electroless plating. *J. Phys. E: Sci. Instrum.*, vol 12, 1979 pp 1015-1022, discusses evaporation with or without oxidation to plate the exterior of a parallel-plate electron multiplier. 15

In order to address the problems of the prior art, according to the present invention, there is provided a method of forming a continuous dynode for a channel electron multiplier or microchannel plate, comprising the steps of:

20 forming a substrate providing a channel surface; and,  
forming on the channel surface at least one thin film to produce in some combination a current carrying portion and an electron emissive portion, characterised in that:  
said thin film is produced by oxidation or nitridation or by a surface reaction with an agent, said agent being formed by chemical vapour deposition at reduced pressure or liquid phase deposition.

25 Examples of methods according to the present invention will now be described with reference to the accompanying drawings, in which:-

Fig. 1 is a fragmentary schematic illustration in perspective of a channel electron multiplier (CEM) according to the prior art;  
30 Fig. 2 is a fragmentary schematic illustration in perspective of a microchannel plate (MCP) according to the prior art;  
Fig. 3 is a side sectional schematic illustration of a reduced lead silicate glass (RLSG) dynode according to the prior art;  
Fig. 4 is a side sectional schematic illustration of a thin film continuous dynode according to one embodiment of the present invention employing a dielectric substrate;  
35 Fig. 5 is a side sectional schematic illustration of a thin film dynode according to another embodiment of the present invention employing a semiconductive substrate;  
Fig. 6 is a side sectional schematic illustration of a thin film dynode according to another embodiment of the present invention employing a conductive substrate;  
Fig. 7 is a side sectional schematic illustration of a thin film dynode according to another embodiment of the present 40 invention employing a lead silicate glass substrate and RLSG semiconductive layer;  
Fig. 8 is a fragmentary schematic side sectional illustration of a curved channel electron multiplier employing a thin film dynode according to the present invention which is shown in an enlarged portion of the drawing;  
Fig. 9 is a fragmentary schematic side sectional illustration of a microchannel plate employing a thin film dynode according to the present invention which is shown in the enlarged portion;  
45 Fig. 10 is a schematic illustration in perspective of a magnetic electron multiplier employing a thin-film dynode according to the present invention which is shown in the enlargement portion;  
Figs. 11 is a plot of signal gain versus electric field strength for exemplary straight-channel electron multipliers with different aspect ratios employing a thin-film dynode according to the present invention;  
Fig. 12 is a plot of signal gain versus bias voltage for exemplary straight-channel electron multipliers of different 50 electrical resistance employing a thin-film dynode according to the present invention;  
Fig. 13 is a plot of signal gain versus bias voltage at different input current levels for an exemplary curved-channel electron multiplier employing a thin-film dynode according to the present invention; and  
Fig. 14 is a plot of the pulse height distribution of a magnetic electron multiplier employing a thin-film dynode of the present invention.

55 The invention is directed to continuous dynodes formed by thin film processing techniques. According to one embodiment of the invention, a continuous dynode is disclosed in which at least one layer is formed by reacting a vapour in the presence of a substrate at a temperature and pressure sufficient to result in chemical vapour deposition

kinetics dominated by interfacial processes between the vapour and the substrate. In another embodiment the surface of a substrate or surface of a thin film previously deposited on a substrate is subjected to a reactive atmosphere at a temperature and pressure sufficient to result in a reaction modifying the surface. In yet another embodiment a continuous dynode is formed in part by liquid phase deposition of a dynode material into the substrate from a supersaturated solution. The resulting devices exhibit conductive and emissive properties suitable for electron multiplication in CEM, MCP and MEM applications.

According to one embodiment of the present invention current carrying (e.g. semiconductive) and dielectric thin films may be vapour deposited along the walls of capillary channels within suitable substrates to yield continuous dynodes which replicate the function of reduced lead silicate glass (RLSG) dynodes. Such devices may be comprised of thin film dynodes that are supported by dielectric or semiconductive substrates in the configuration of CEMs and MCPs. For electrically insulating substrates, deposition of both a current carrying or semiconductive layer and an electron emissive layer would generally be necessary; however, appropriately semiconductive substrates would only require the deposition of an emissive layer.

An example of a continuous thin-film dynode 60, according to one embodiment of the present invention, is illustrated in Fig. 4. The dynode 60 comprises an emissive layer or film 62, a semiconductive layer or film 64 and a dielectric substrate 66. The dynode 60 is formed by depositing the semiconductive film such as silicon to a thickness  $t$  in the range of 10-1000 nm onto the surface 70 of the substrate 66 such as silica glass. By controlling the concentration of a suitable dopant (e.g., phosphorous) and the morphology of the film, a silicon semiconductive layer 64 with, for instance,  $t \approx 100$  nm can thus be obtained with resistivity  $r = 10^1 - 10^3 \Omega \cdot \text{cm}$  yielding  $R_s = r/t = 10^6 - 10^8 \Omega/\text{sq}$  for CEM dynodes, or  $r = 10^6 - 10^7 \Omega \cdot \text{cm}$  giving  $R_s \approx 10^{11} - 10^{12} \Omega/\text{sq}$  for MCP dynodes. Other silicon semiconductive films with higher resistivities in the range of  $r = 10^7 - 10^9 \Omega \cdot \text{cm}$ , yielding  $R_s = 10^{12} - 10^{14} \Omega/\text{sq}$  for MCP dynodes, may be prepared by incorporation of other dopants to form semi-insulating films (e.g., SIPOS).

In a preferred embodiment deposition is achieved by a chemical vapour deposition (CVD) technique. As used and understood herein, the term CVD refers to the formation of thin films under conditions which are generally controlled by interfacial processes between gaseous reactants or reaction products and the substrate rather than by the transport of chemical species through the gas phase near the surface of the substrate.

In the embodiment illustrated in Fig. 4, the emissive layer 62 may comprise a thin layer of  $\text{SiO}_2$ , a native oxide about 2-5 nm in thickness  $d$ , overlying the silicon semiconductive layer 64, and be formed by exposure of the semiconductor surface 68 to ambient. Alternatively, the emissive layer 62 may be formed or grown to a thickness of 2-20 nm by oxidation or nitridation of the semiconductor surface 68 at elevated temperatures in the presence of reactive gases (e.g.,  $\text{O}_2$  or  $\text{NH}_3$ ). As another alternative, an emissive film 62 such as  $\text{MgO}$  with higher secondary electron yield than  $\text{SiO}_2$  for electron energies  $E_p$  of interest may be deposited by a CVD process to a thickness  $d = 2-20$  nm upon the surface 68 of semiconductive layer 64 to form the basic two-layer structure of the thin film dynode 60. For  $\text{SiO}_2$ , if  $E_p^I \sim 40$  eV and  $6\delta \sim E_p/E_p^I$ , then  $0.5 \leq \delta \leq 2.5$  for 20 eV  $\leq E_p \leq 100$  eV; whereas for  $\text{MgO}$ , if  $E_p^I \sim 25$  eV, then  $0.8 \leq \delta \leq 4$  for the same range of  $E_p$ . As an alternative to dielectric emissive layers, semiconductive films with surfaces exhibiting negative electron affinity, and thus highly efficient secondary electron emission, may also be formed by CVD methods (e.g.,  $\text{GaP:Cs-O}$ ,  $\text{GaP:Ba-O}$ ,  $\text{GaAs:Cs-O}$ ,  $\text{InP:Cs-O}$  and  $\text{Si:Cs-O}$ ).

Generally, the thickness  $t$  and resistivity  $r$  of the semiconductive layer 64 (and therefore sheet resistance  $R_s = r/t$ ) should be uniform along the length of a thin-film dynode 60 to provide a constant electric field in which to accelerate multiplying electrons. Also, the secondary electron yield  $\delta$  of the emissive layer 62 should be sufficiently high and spatially uniform to produce adequate signal gain with good multiplication statistics. However, if desired, the layers 62, 64 may be formed in radially graded or longitudinally staged CVD applications in order to produce a continuous thin film dynode having graded properties throughout its thickness or incrementally staged properties along its length, respectively. Also, although not always noted in detail, modification of the surface of a bulk semiconductor substrate or a deposited thin film to achieve suitable electron emissive properties may be effected by subsequent oxidation or nitridation.

Substrates for CEMs and MCPs can be either electrically insulating or semiconductive. Insulating substrates 66 (i.e.,  $r \geq 10^{12} \Omega \cdot \text{cm}$ ) would generally require deposition of both the electronically semiconductive layer 64 and the electron emissive layer 62 to form the efficient thin-film dynode 60 (Fig. 4).

In contrast, and in accordance with another embodiment of the present invention shown in Fig. 5, the continuous dynode 72 comprises an emissive layer 62 such as  $\text{MgO}$  deposited on the surface 78 of a suitably semiconductive substrate 76, where  $r = 10^5-10^7 \Omega \cdot \text{cm}$  for a CEM and  $r = 10^8-10^{11} \Omega \cdot \text{cm}$  for an MCP. The bias current for the dynode 72 could be carried throughout the bulk of the substrate 76. Also, as shown in the embodiment illustrated in Fig. 6, a dynode 80 having a somewhat more conductive substrate 82 could be employed by first depositing a dielectric isolation layer 84 (e.g., a film of  $\text{SiO}_2$  formed by liquid phase deposition from a supersaturated solution) having thickness ( $z$ ) = 2-5  $\mu\text{m}$  on the substrate 82 prior to formation of the semiconductive 64 and electron emissive 62 layers.

Use of insulating 66 or electrically-isolated 82 substrates as in Figs. 4 and 6 for fabrication of thin film electron multipliers by deposition of conductive and emissive layers is the preferred embodiment of this invention. Greater

flexibility in the selection of electrical properties for a given device and likely better control of such properties during manufacture are major advantages of this approach. However, for certain applications (e.g., reduction of positive ion feedback), the bulk conductive device 72 of Fig. 5 might hold particular attraction.

In current manufacturing practice, multi-component lead silicate glass surfaces are chemically and thermally processed to produce continuous RLSG dynodes with appropriate electrical and secondary emission characteristics (Fig. 3). However, in another embodiment of the present invention, illustrated in Fig. 7 the RLSG dynode 90 is comprised of a dielectric emissive layer 62 and an underlying semiconductive layer 54. This two-layer structure is mechanically supported by the lead silicate base glass 56 in channel geometries which are characteristic of CEMs or MCPs. The emissive layer 62 in contrast to prior RLSG dynodes (Fig. 3) is preferably formed by CVD of an appropriate material such as  $\text{Si}_3\text{N}_4$ ,  $\text{MgO}$ , or the like. The semiconductive layer 54 may be formed by  $\text{H}_2$  reduction under conditions sufficient to promote formation of the semiconductive layer but minimize the formation of emissive layer 52, as in conventional RLSG dynodes (Fig. 3).

Further, when used as an emissive layer 62 in any of the embodiments of Figs. 4-7,  $\text{Si}_3\text{N}_4$  acts as a hermetic seal to protect the underlying surfaces from environmental degradation thereby enhancing the product shelf life.  $\text{Si}_3\text{N}_4$  and  $\text{Al}_2\text{O}_3$  are also more resistant than  $\text{SiO}_2$  or  $\text{SiO}_2$ -rich glasses to degradation under electron bombardment thereby extending the operational lifetime of the dynode.

Exemplary devices employing thin film dynodes in accordance with the embodiment of Fig. 4 are illustrated in Figs. 8-10. It should be understood, however, that any of the aforementioned alternative embodiments of thin film dynodes illustrated in Figs. 5-7 may also be employed with the exemplary embodiments of Figs. 8-10. In Fig. 8 a CEM 100 is illustrated which is formed of a curved capillary glass tube 102 having a flared input end 104 and a straight output end 106. If desired, the tube 102 may be formed of a moulded and sintered dielectric block of ceramic or glass. Electrodes 108 are formed on the exterior of the tube 102 and thin-film dynode 110 is formed on the interior of the tube as shown. In accordance with the invention the tube 102 is first subjected to a two-stage CVD process whereby the respective exterior and interior surfaces 114 and 112 are successively coated in a reactor (not shown) with a semiconductive layer 64 and emissive layer 62 which are shown in the enlargement. The exterior of the tube 102 is masked and stripped (e.g., by sandblasting or etching) to produce a nonconductive band 118 on the exterior wall 114. Metal electrodes 108 are thereafter applied by a suitable evaporation procedure. The semiconductive layer 64 and emissive layer 62 in the internal surface 112 functions as the continuous thin film dynode 110.

In Fig. 9 an MCP 120 is illustrated which comprises a dielectric ceramic or glass substrate 122 formed with micro-channels 124 and electrodes 126 deposited on the opposite faces 128 of the substrate 122. Thin-film dynodes 130 formed of an emissive layer 62 and a semiconductive layer 64 as hereinbefore described are deposited on the walls 132 of the channels 124. (Portions of the films 62, 64 which coat the substrate 122 elsewhere do not function as a dynode.) The electrodes 126 are deposited atop the films (62,64) on the flat parallel faces 128 of the substrate 122. In accordance with the invention, the MCP 120 may be formed by the GMD process described above or by an anisotropic etching technique described in the said copending application>.

In Fig. 10 a magnetic electron multiplier (MEM) 140 is illustrated which is formed, in part, by a pair of glass plates 142 or other suitable dielectric substrate having electrodes 144 on the ends 146 and thin-film dynodes 148 on the confronting surfaces 150. The dynode 148 is formed of an emissive layer 62 and a semiconductive layer 64 as hereinbefore described. The electrodes 144 are deposited after stripping the exterior surfaces 151 to remove films (62,64).

The process of forming thin-film continuous dynodes according to the present invention in capillary channels of macroscopic to microscopic dimensions for CEMs and MCPs follows. Chemical vapour deposition (CVD) according to one embodiment of the present invention is a method by which thin solid films of suitable materials (e.g. semiconductors or ceramics) are vapour deposited onto the surface of a substrate by reaction of gaseous precursors. Temperature, pressure, and gaseous reactants are selected and balanced so that the physical structure and electrical and electron emissive properties of the dynodes so produced are appropriate for achieving the performance desired. In thermally-activated CVD processes, the substrate is typically heated to a temperature ( $T = 300\text{-}1200^\circ\text{C}$ ), that is sufficient to promote the deposition reaction; however, such reactions can also be plasma-assisted or photochemically-activated at even lower temperatures. Basic deposition reactions include pyrolysis, hydrolysis, disproportionation, oxidation, reduction, synthesis reactions and combinations of the above. According to the invention, low pressure CVD (LPCVD) occurring preferably at pressures less than 1300 Pa (10 torr) and more desirably between about 130 and 13 Pa (1 and 0.1 torr), results in the formation of a satisfactory continuous thin film dynode. Generally, LPCVD results in conformal thin-films usually having substantially uniform geometrical, electrical and electron emissive properties. The deposition reactions preferably occur heterogeneously at the substrate surface rather than homogeneously in the gas phase. Metal hydrides and halides as well as metal organics are common vapour precursors.

Physical properties of CVD thin films are a function of both the composition and structure of the deposit. The range of materials that has been produced by CVD methods is quite broad and includes the following: common, noble, and refractory metals (e.g., Al, Au, and W); elemental and compound semiconductors (e.g., Si and GaAs); and ceramics and dielectrics (e.g., diamond, borides, nitrides, and oxides). Properties of such thin-film materials can be varied sig-

nificantly by incorporation of suitable dopants, or by control of morphology. The morphology of CVD materials can be single crystalline, polycrystalline, or amorphous depending on the processing conditions and the physicochemical nature of the substrate surface. Also, materials of exceptional purity can be prepared by CVD techniques.

In general, the emissive portion of the dynodes of the present invention may be formed of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{SnO}_2$ ,  $\text{BaO}$ ,  $\text{Cs}_2\text{O}$ ,  $\text{Si}_3\text{N}_4$ ,  $\text{Si}_x\text{O}_y\text{N}_z$ , C (Diamond), BN, and AlN; negative electron affinity emitters GaP:Cs-O, GaP:Ba-O, GaAs:Cs-O, InP:Cs-O, and Si:Cs-O. Such materials may be formed from precursors such as  $\text{SiH}_4$ ,  $\text{SiCl}_x\text{H}_y$ ,  $\text{Si}(\text{OC}_2\text{H}_5)_4$ ,  $\beta$ -diketonate compounds of Al (e.g.,  $\text{Al}(\text{C}_5\text{HO}_2\text{F}_6)_3$ ),  $\text{Al}(\text{CH}_3)_3$ ,  $\beta$ -diketonate compounds of Mg (e.g.,  $\text{Mg}(\text{C}_5\text{HO}_2\text{F}_6)_2$ ),  $\text{SnCl}_4$ ,  $\beta$ -diketonate compounds of Ba (e.g.,  $\text{Ba}(\text{C}_{11}\text{H}_{19}\text{O}_2)_2$ ),  $\text{CH}_4$ , Cs,  $\text{B}_2\text{H}_6$ ,  $\text{Ga}(\text{C}_2\text{H}_5)_3$ ,  $\text{Ga}(\text{CH}_3)_3$ ,  $\text{PH}_3$ ,  $\text{AsH}_3$ , In ( $\text{CH}_3)_3$ ,  $\text{O}_2$ ,  $\text{N}_2\text{O}$ , NO,  $\text{N}_2$ , and  $\text{NH}_3$ . The current carrying portion of the dynodes according to the present invention may be formed of As-, B-, or P-doped Si, Ge (undoped), Si (undoped),  $\text{SiO}_x$  (SIPOS),  $\text{Si}_x\text{N}_y$ ,  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ , and  $\text{SnO}_x$ . Precursors for such materials may be  $\text{SiH}_4$ ,  $\text{PH}_3$ ,  $\text{GeH}_4$ ,  $\text{B}_2\text{H}_6$ ,  $\text{AsH}_3$ ,  $\text{SnCl}_4$ ,  $\text{Ga}(\text{C}_2\text{H}_5)_3$ ,  $\text{Ga}(\text{CH}_3)_3$ ,  $\text{Al}(\text{CH}_3)_3$ ,  $\text{N}_2\text{O}$ ,  $\text{N}_2$ , and  $\text{NH}_3$ .

Selected representative examples of semiconductive and dielectric materials and their precursors which are of particular interest for fabrication of thin-film dynodes by CVD methods are given in Tables I and II, respectively. Table I lists representative materials with ranges of electrical resistivity  $r$  at  $25^\circ\text{C}$  that, assuming a film thickness of  $t = 100$  nm, yield suitable ranges of sheet resistance  $R_s$  for the semiconductive layer 64 of a continuous dynode in either a CEM or MCP.

TABLE I

<u>Materials for Semiconductive Layer (<math>t = 100</math> nm)</u>				
Material	Precursor	$r(\Omega\cdot\text{cm})$	$R_s(\Omega/\text{sq})$	Device
Si (P-doped)	$\text{SiH}_4$ and $\text{PH}_3$	$10^1\text{-}10^3$	$10^6\text{-}10^8$	CEM
Ge (undoped)	$\text{GeH}_4$	$10^1\text{-}10^2$	$10^6\text{-}10^7$	CEM
Si (undoped)	$\text{SiH}_4$	$10^6\text{-}10^7$	$10^1\text{-}10^{12}$	MCP
$\text{SiO}_x$ (SIPOS)	$\text{SiH}_4$ and $\text{N}_2\text{O}$	$10^7\text{-}10^9$	$10^{12}\text{-}10^{14}$	MCP
$\text{Si}_x\text{N}_y$	$\text{SiH}_4$ and $\text{NH}_3$	$10^6\text{-}10^9$	$10^{11}\text{-}10^{14}$	MCP

Table II identifies representative materials for use as the emissive layer 62 with sufficiently low values of  $E_p^{-1}$  to produce adequate or high values of secondary electron yield  $\delta$  in the electron energy range of  $20\text{eV} \leq E_p \leq 100\text{eV}$ .

TABLE II

<u>Materials for Emissive Layer (<math>20\text{eV} \leq E_p \leq 100\text{eV}</math>)</u>			
Material	Precursor	$E_p^{-1}$ (eV)	$\delta=E_p/E_p^{-1}$
$\text{SiO}_2$ glass	$\text{SiH}_4$ or $\text{Si}(\text{OC}_2\text{H}_5)_4$ and $\text{O}_2$	$\sim 40$	$\sim 0.5\text{-}2.5$
$\text{Al}_2\text{O}_3$	$\text{Al}(\text{CH}_3)_3$ or $\text{Al}(\text{C}_5\text{HO}_2\text{F}_6)_3$ and $\text{O}_2$	$\sim 25$	$\sim 0.8\text{-}4$
MgO	$\text{Mg}(\text{C}_5\text{HO}_2\text{F}_6)_3$ and $\text{O}_2$	$\sim 25$	$\sim 0.8\text{-}4$
GaP:Cs-O	$\text{Ga}(\text{CH}_3)_3$ , $\text{PH}_3$ , Cs, and $\text{O}_2$	$\sim 20$	$\sim 1\text{-}5$

While thermally-activated CVD may be practised in a reactor (not shown) at atmospheric pressure (APCVD), important advantages are gained by reducing the reactor pressure ( $P$ ) to the range of about  $13\text{ Pa}$  (0.1 torr)  $< P < 1.3 \times 10^3\text{ Pa}$  (10 torr). When  $P$  is decreased from about  $1.0 \times 10^5\text{ Pa}$  (760 torr) to  $1.3 \times 10^2\text{ Pa}$  (1 torr), the mean free path of gas molecules at  $T = 600^\circ\text{C}$  increases a thousandfold from about  $0.2\text{ }\mu\text{m}$  to  $200\text{ }\mu\text{m}$ . In low pressure, thermally-activated CVD (LPCVD), the resulting higher diffusivities of the reactant and product gasses cause the film growth rate to be controlled by kinetic processes at the gas-substrate interface (e.g., adsorption of reactants, surface migration of adatoms, chemical reaction, or desorption of reaction products) rather than by mass transport of the gasses through a stagnant boundary layer adjacent to the interface. By maintaining the surface of a substrate at constant temperature  $T = 300\text{-}1200^\circ\text{C}$ , conformal films can be heterogeneously deposited by LPCVD even over substantial contours because supply of an equal reactant flux to all locations on the substrate is not critical under surface reaction rate-limited conditions. Conformal coverage of films over complex topographies (e.g., along a trench or channel) depends on rapid migration of adatoms prior to reaction. In the case of APCVD, however, lower gas diffusivities promote mass transport-limited conditions where an equal reactant flux to all areas of the substrates is essential for film uniformity.

For this reason, LPCVD is thought to have a greater potential than APCVD for attaining the objective of depositing conformal conductive and emissive layers 64,62 with uniform thicknesses and properties within capillary substrate geometries to form thin-film dynodes for CEMs and MCPs. Also, since LPCVD can provide conformal films without the

substrate 66 being in the line-of-sight of the vapour source, it is clearly superior to physical vapour deposition methods (e.g., evaporation and sputtering) for this application. Other noteworthy advantages of LPCVD include better compositional and structural control, lower deposition temperatures, fewer particulates due to homogeneous reactions, and lower processing costs.

5 As an alternative to thermally-activated LPCVD, plasma-assisted CVD at low pressure (PACVD) is attractive because it offers an even lower range of processing temperatures ( $T = 25\text{--}500^\circ\text{C}$ ) than LPCVD and the considerable potential for synthesizing unusual thin-film materials under non-equilibrium conditions. Photochemically-activated CVD (PCCVD) is another low temperature processing variant of interest.

10 If a graduation in film thickness along the length of a channel is desired, the pressure may be raised to reduce gas transport and promote nonuniform deposition along the channel axis without departing from the invention. Likewise, staged deposition may be achieved by producing one or more continuous, interconnected thin-film dynode elements, each being uniform over a substantial length. Also, the deposition parameters may be held constant or varied gradually so that, respectively, a single compositionally uniform film is deposited which desirably exhibits both conductive and emissive properties, or the composition and properties of the film or films vary with thickness to achieve some desirable purpose.

15 Aside from electrical requirements, substrates for CEMs and MCPs should be comprised of materials that are readily formable into the geometries of such devices but also compatible with CVD processing methods. Contemplated deposition temperatures of  $300\text{--}1200^\circ\text{C}$  for LPCVD require a substrate to be sufficiently refractory so that it does not melt or distort during processing. In addition, the substrate should be chemically and mechanically suited to the overlying thin films such that deleterious interfacial reactions and stresses are avoided. Moreover, the substrate should be made of a material with adequate chemical purity such that control over the deposition process and essential properties of the thin-film dynodes are not compromised by contamination effects. Finally, for electron multipliers that operate at a high bias current, substrates with high thermal conductivity ( $k$ ) would assist the dissipation of Joule heat.

20 In accordance with the present invention, the substrate may be a material selected from the group consisting of  $\text{Si}_3\text{N}_4$ , AlN,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  glass,  $\text{R}_2\text{O}\text{-}\text{Al}_2\text{O}_3\text{-}\text{SiO}_2$  ( $\text{R} = \text{Li}, \text{Na}, \text{K}$ ) glasses,  $\text{R}_2\text{O}\text{-}\text{BaO}\text{-}\text{Bi}_2\text{O}_3\text{-}\text{PbO}\text{-}\text{SiO}_2$  ( $\text{R} = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ ) glasses, AlAs, GaAs, InP, GaP, Si, Si with a  $\text{SiO}_2$  isolation layer, and GaAs or InP with a  $\text{Si}_3\text{N}_4$  isolation layer.

25 Selected representative examples of refractory, high purity materials suitable for substrates 66, 76, 82 are given in Table III with nominal values of bulk electrical resistivity  $r$  and thermal conductivity  $k$  at  $25^\circ\text{C}$ .

30

TABLE III

Substrate Materials			
Material	$r$ ( $\Omega\text{.cm}$ )	$k$ ( $\text{W/m}\cdot^\circ\text{K}$ )	Device(Substrate)
AlN	$>10^{14}$	>150	CEM (66) and MCP (66)
$\text{Al}_2\text{O}_3$	$>10^{14}$	20	CEM (66) and MCP (66)
$\text{SiO}_2$ glass	$>10^{14}$	1	CEM (66) and MCP (66)
Si (undoped) with $\text{SiO}_2$ isolation layer	$>10^{12}$	--	MCP (82)
GaP (undoped)	$\sim 10^{10}$	--	MCP (76)
GaAs (undoped)	$\sim 10^8$	46	MCP (76)
Si (undoped)	$\sim 10^5$	150	CEM (76)

35 A dielectric substrate for a CEM can be produced, for instance, by thermal working of fused quartz glass or by injection moulding and sintering of ceramic powders of  $\text{Al}_2\text{O}_3$  or AlN. The use of lithographic methods and etching with a flux of reactive particles to create an array of anisotropically etched hollow channels in wafer-like substrates of materials such as  $\text{SiO}_2$ , Si, or GaAs for MCPs is also possible as described in our copending application noted above.

40 According to the invention, vapour deposition methods based on CVD can be used to fabricate continuous thin-film dynodes with electrical and electron emissive properties that are comparable to those obtained with conventional RLSG dynodes. Because of this, more efficient manufacturing procedures for CEMs and MCPs are available, including improvements in RLSG configurations. Further, it is expected that significant improvements in the performance of CEMs and MCPs made in accordance with the teachings of the present invention can be achieved by capitalizing on the ability to tailor the materials and structure of thin-film dynodes.

45 The advantages which may be achievable include better multiplication statistics and operation at a lower external bias potential  $V_B$  by deposition of an emissive layer 62 with higher secondary electron yield  $\delta$  than conventional RLSG dynodes (e.g., MgO or negative electron affinity emitters such as GaP:Cs-O). Better gain stability and longer operational lifetimes (e.g.,  $\geq 100 \text{ C/cm}^2$  of extracted charge) are achievable by use of an emissive layer 62 such as  $\text{Si}_3\text{N}_4$  or  $\text{Al}_2\text{O}_3$  which exhibits low susceptibility to outgassing or degradation by electron irradiation. Improved noise characteristics and extended dynamic range result from choice of high-purity materials for dynodes and substrates which are free of

radioactive impurities, a major source of background noise. Maximum operating temperatures approaching 500°C are achieved by use of suitably refractory materials for dynodes and substrates. Environmental stability is enhanced by application of an emissive layer 62 (e.g., Si<sub>3</sub>N<sub>4</sub>) that can also function as a hermetic seal for environmentally sensitive dynode materials such as RLSG. Very importantly, the current transfer characteristics for specific applications may be optimized by exercising control over the physical dimensions, composition and morphology, and hence the electrical and electron emissive properties of the films 62,64.

Thin-film processing according to the present invention includes the surface treatment of deposited or bulk semiconductor materials to achieve desirable electron emissivity. In embodiments referred to in Figs. 4 and 6 the surface 68 of a semiconductive layer 64 such as silicon may be oxidized (or nitrided) at 300-1200°C in O<sub>2</sub> (or NH<sub>3</sub>) to produce an emissive layer 62 of SiO<sub>2</sub> (or Si<sub>3</sub>N<sub>4</sub>) with thickness d = 2-20 nm. In Fig. 5 a bulk semiconductor 76 such as silicon may be treated in a similar manner to produce an emissive surface. Also, dielectric films such as SiO<sub>2</sub> may be formed by liquid phase deposition (LPD) to form the emissive layer 62 or the isolation layer 84 in the embodiments of Figs. 4-7. Using LPD, for instance, SiO<sub>2</sub> films can be deposited at 25-50°C onto the interior surfaces of macroscopic or microscopic capillary channels of CEMs or MCPs from a supersaturated aqueous solution of H<sub>2</sub>SiF<sub>6</sub> and SiO<sub>2</sub> with a small addition of H<sub>3</sub>BO<sub>3</sub>. The above processes may be combined with other processes herein described to produce various continuous thin-film dynode configurations.

Examples which describe fabrication and performance of CEM and MEM devices prepared in accordance with the present invention are set forth below.

#### Example I

Fused quartz capillary tubes (1 mm ID x 3 mm OD) with one end flared into an input cone, similar to the tube 102 illustrated in Fig. 8, were employed as substrates to make sets of straight-channel CEMs with  $\alpha = L/D = 20, 30$ , and 40, and curved-channel CEMs with  $\beta = L/S = 1.2$ .

The substrates were first cleaned by a standard procedure and then placed inside a hot-wall, horizontal-tube, LPCVD reactor for deposition of silicon thin films. Amorphous undoped silicon films were formed on one set of substrates by reaction of SiH<sub>4</sub> at P = 26-52 Pa (0.2-0.4 torr) and T = 540-560°C. In a separate experiment, amorphous P-doped silicon films were formed on another set of substrates by reaction of PH<sub>3</sub> and SiH<sub>4</sub> in a reactant ratio of PH<sub>3</sub>/SiH<sub>4</sub> = 5 x 10<sup>-4</sup> under otherwise similar conditions. Semiconductive films 64 of thickness t = 300 nm were thus deposited on surfaces 112,114 of capillary substrates 102 (Fig. 8) at a rate of 1-10 nm/min.

After deposition of the silicon films, the capillary substrates were allowed to cool in the reactor and then were assembled into CEMs 100 as follows. Electrical continuity along the outer surface 114 of the capillary tubes was broken by removing the silicon deposit within a narrow band 118 around this outer surface (Fig. 8). Nichrome electrodes 108 were then vacuum-evaporated onto the ends of each tube without coating the non-conductive band between them.

Each CEM was completed by attaching electrical leads to both electrodes.

Measurements of electrical resistance down the bore of the straight-channel CEMs showed that the undoped and P-doped silicon films had sheet resistances R<sub>s</sub> ≈ 10<sup>11</sup> Ω/sq and ≈ 10<sup>8</sup> Ω/sq, respectively. In both cases, R<sub>s</sub> was independent of channel geometry for 20 ≤ α ≤ 40. These results indicate that both the thickness and resistivity of each film, as prepared by LPCVD methods, are substantially uniform along the length of capillary channels with aspect ratios sufficient to support useful electron multiplication.

Methods for characterizing the gain G of electron multipliers in analog and pulse counting modes are known. Plots of analog gain G = I<sub>o</sub>/I<sub>i</sub> versus electric field strength ε applied to straight-channel CEMs 100 having α = 20, 30, and 40 with R<sub>s</sub> ≈ 10<sup>8</sup> Ω/sq for input currents I<sub>i</sub> = 1 pA are presented in Fig. 11. While unsaturated gains G ≥ 10<sup>4</sup> were obtained for each CEM, one also sees the G increases with α at sufficiently large values of ε.

Graphs of analog gain G = I<sub>o</sub>/I<sub>i</sub> versus bias voltage V<sub>B</sub> for straight-channel CEMs 100 having R<sub>s</sub> ≈ 10<sup>11</sup> Ω/sq and ≈ 10<sup>8</sup> Ω/sq with α = 40 for I<sub>i</sub> = 1 pA are given in Fig. 12. The CEM with higher R<sub>s</sub> shows a saturated gain G = 10<sup>3</sup>-10<sup>4</sup> and is limited by the relatively low bias current i<sub>B</sub> that is carried in the semiconductive layer. In contrast, the CEM with lower R<sub>s</sub> exhibits an unsaturated gain G > 10<sup>4</sup>.

Fig. 13 displays plots of analog gain G = I<sub>o</sub>/I<sub>i</sub> versus voltage for a curved-channel CEM 100 with β = 1.2 and R<sub>s</sub> ≈ 10<sup>8</sup> Ω/sq for several values of I<sub>i</sub> = 1, 10, and 100 pA. Saturated gains are observed at all input levels I<sub>i</sub>. In particular, the roughly order of magnitude decreases in saturated gain with corresponding increases in I<sub>i</sub> clearly indicate a current-limited multiplier response. For I<sub>i</sub> = 1 pA, this CEM shows a maximum gain G > 10<sup>6</sup>.

#### Example II

Fused quartz plates (25 x 60 x 1 mm) similar to the plates 142 that are illustrated in Fig. 10, were used as substrates to form thin-film dynodes for a MEM 140. Amorphous P-doped silicon films with t ≈ 300 nm and R<sub>s</sub> ≈ 10<sup>8</sup> Ω/sq were formed on the planar substrates 142 using methods and conditions similar to those described in Example I for the CEMs.

The MEM was assembled as follows. The silicon deposit was removed from one flat surface 151. A pattern of nichrome electrodes was then deposited through a mask (not shown) onto the other side of each plate 142 with the silicon deposit 148. A set of two plates 142 with closely matched  $R_s$  were used as field and dynode strips to construct the MEM 140.

5 Pulse counting measurements on the MEM 140 yielded the pulse height distribution given in Fig. 14. The distribution shown represents the number of output pulses as a function of gain, relative to a calibration line of  $G = 10^7$ . When operated at a bias voltage  $V_B = 2500$  V, the MEM 140 exhibited a negative exponential pulse height distribution with a maximum gain in the range of  $10^6 - 10^7$ .

10 The structure of the thin-film dynodes in the above described CEMs 100 and MEM 140 of Examples I and II approximates the embodiment depicted in Fig. 4. A native oxide of  $\text{SiO}_2$  with thickness  $d = 2-5$  nm serves as the emissive layer 62 and overlies a silicon semiconductive layer 64, which are both supported by a fused quartz substrate 66. The feasibility of such thin film dynodes to support practical levels of electron multiplication has clearly been established by the foregoing Examples. Further, the ability to tailor the current transfer characteristics of an electron 15 multiplier by adjusting the current-carrying properties of a thin-film dynode has been demonstrated. Also, the formation and control of semiconductive films 64 with electrical properties which are suitable for single-channel devices (e.g., P-doped silicon with  $R_s \approx 10^8 \Omega/\text{sq}$ ) as well as for multi-channel ones (e.g., undoped silicon with  $R_s \approx 10^{11} \Omega/\text{sq}$ ) have been shown. Finally, one notes that while the signal gains of thin-film devices in Examples I and II approach those of comparable RLSG devices, the performance of the former could be improved by forming a somewhat thicker emissive 20 layer 62 by thermal oxidation or nitridation reactions or by depositing an emissive layer 62 such as  $\text{MgO}$  with better secondary electron emission characteristics than  $\text{SiO}_2$ .

### Claims

- 25 1. A method of forming a continuous dynode for a channel electron multiplier or microchannel plate, comprising the steps of:
- forming a substrate (66) providing a channel surface; and,  
 30 forming on the channel surface at least one thin film to produce in some combination a current carrying portion (64) and an electron emissive portion (62), characterised in that:  
 said thin film is produced by oxidation or nitridation or by a surface reaction with an agent, said agent being formed by chemical vapour deposition at reduced pressure or liquid phase deposition.
- 35 2. A method according to claim 1, wherein the thin film is formed by chemical vapour deposition (CVD), including the step of reacting a vapour in the presence of the substrate at a temperature and at a pressure selected to result in CVD kinetics which are dominated by interfacial processes between the vapour and the substrate.
- 40 3. The method of claim 2, further comprising forming at least one channel in the substrate having a high aspect ratio for deposition of the dynode therein.
- 45 4. The method of claim 3, further comprising forming the dynode conformally on the channel wall along at least a selected length thereof.
- 50 5. The method of any of claims 2 to 4, wherein the temperature  $T$  is  $300^\circ\text{C} \leq T \leq 1200^\circ\text{C}$ .
- 55 6. The method of any of claims 2 to 5, wherein the pressure is below 1300 Pa (10 torr).
7. The method of claim 6, wherein the pressure is below 130 Pa (1 torr).
8. The method of claim 7, wherein the pressure is between 130 and 13 Pa (1 torr and 0.1 torr).
9. The method of any of claims 1 to 8, wherein the substrate comprises a material selected from the group consisting of  $\text{Si}_3\text{N}_4$ , AlN,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  glass,  $\text{R}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$  ( $\text{R} = \text{Li}, \text{Na}, \text{K}$ ) glasses,  $\text{R}_2\text{O}-\text{BaO}-\text{Bi}_2\text{O}_3-\text{PbO}-\text{SiO}_2$  ( $\text{R} = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ ) glasses, AlAs, GaAs, InP, GaP, Si, Si with a  $\text{SiO}_2$  isolation layer, and GaAs or InP with a  $\text{Si}_3\text{N}_4$  isolation layer.
10. The method of any of claims 1 to 9, wherein the electron multiplier is a microchannel plate and the substrate materials have a resistivity  $r \geq 10^8 \Omega\cdot\text{cm}$ .

11. The method of any of claims 1 to 9, wherein the electron multiplier is a CEM and the substrate has a resistivity  $r$  of  $10^5 \Omega\text{-cm} \leq r \leq 10^8 \Omega\text{-cm}$ .
- 5      12. The method of any of claims 1 to 9, wherein the electron multiplier is a CEM or MEM and the substrate has a resistivity  $r \geq 10^{12} \Omega\text{-cm}$ .
13. The method of any of claims 1 to 12, wherein the emissive portion comprises a thin film of one or more materials selected from the group consisting of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{SnO}_2$ ,  $\text{BaO}$ ,  $\text{Cs}_2\text{O}$ ,  $\text{Si}_3\text{N}_4$ ,  $\text{Si}_x\text{O}_y\text{N}_z$ , C (Diamond), BN and AlN; negative electron affinity emitters  $\text{GaP:Cs-O}$ ,  $\text{GaP:Ba-O}$ ,  $\text{GaAs:Cs-O}$ ,  $\text{InP:Cs-O}$ , and  $\text{Si:Cs-O}$ .
- 10     14. The method of any of claims 1 to 13, wherein the emissive portion comprises a thin film with a thickness of 2 to 20 nm.
- 15     15. The method of any of claims 1 to 14, wherein precursors for the emissive portion include materials selected from the group consisting of  $\text{SiH}_4$ ,  $\text{SiCl}_x\text{H}_y$ ,  $\text{Si}(\text{OC}_2\text{H}_5)_4$ ,  $\beta$ -diketonate compounds of Al (e.g.,  $\text{Al}(\text{C}_5\text{HO}_2\text{F}_6)_3$ ,  $\text{Al}(\text{CH}_3)_3$ ,  $\beta$ -diketonate compounds of Mg (e.g.,  $\text{Mg}(\text{C}_5\text{HO}_2\text{F}_6)_2$ ),  $\text{SnCl}_4$ ,  $\beta$ -diketonate compounds of Ba (e.g.,  $\text{Ba}(\text{C}_{11}\text{H}_{19}\text{O}_2)_2$ ),  $\text{CH}_4$ ,  $\text{Cs}$ ,  $\text{B}_2\text{H}_6$ ,  $\text{Ga}(\text{C}_2\text{H}_5)_3$ ,  $\text{Ga}(\text{CH}_3)_3$ ,  $\text{PH}_3$ ,  $\text{AsH}_3$ ,  $\text{In}(\text{CH}_3)_3$ ,  $\text{O}_2$ ,  $\text{NO}$ ,  $\text{N}_2\text{O}$ ,  $\text{N}_2$ , and  $\text{NH}_3$ .
- 20     16. The method of any of claims 1 to 15, wherein the electron emissive portion has a first crossover energy, at which  $\delta = 1$ , in the range of  $10 \text{ eV} \leq E_p \leq 50 \text{ eV}$ .
- 25     17. The method of any of claims 1 to 16, wherein the current carrying portion comprises a thin film material selected from the group consisting of As-, B-, or P-doped Si, Ge (undoped), Si (undoped),  $\text{SiO}_x$  (SIPoS),  $\text{Si}_x\text{N}_y$ ,  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ , and  $\text{SnO}_x$ .
18. The method of any of claims 1 to 17, wherein the current carrying portion comprises a thin film with a thickness of 10-1000 nm.
- 30     19. The method of any of claims 1 to 18, wherein precursors for the materials forming the current carrying portion comprise materials selected from the group consisting of  $\text{SiH}_4$ ,  $\text{PH}_3$ ,  $\text{GeH}_4$ ,  $\text{B}_2\text{H}_6$ ,  $\text{AsH}_3$ ,  $\text{SnCl}_4$ ,  $\text{Ga}(\text{C}_2\text{H}_5)_3$ ,  $\text{Ga}(\text{CH}_3)_3$ ,  $\text{Al}(\text{CH}_3)_3$ ,  $\text{N}_2\text{O}$ ,  $\text{N}_2$  and  $\text{NH}_3$ .
- 35     20. The method of any of claims 1 to 9 or 12 to 19, wherein the current carrying portion comprises a thin film with a sheet resistance  $R_s$  of  $10^6 \Omega/\text{sq} \leq R_s \leq 10^8 \Omega/\text{sq}$  for channel electron multipliers and magnetic electron multipliers.
21. The method of any of claims 1 to 8 or 10 to 19, wherein the current carrying portion comprises a thin film with a sheet resistance  $R_s$  of  $10^{11} \Omega/\text{sq} \leq R_s \leq 10^{14} \Omega/\text{sq}$  for microchannel plates.
- 40     22. The method of any of claims 1 to 21, wherein first a thin film of a current carrying material and then a thin film of an electron emissive material are deposited onto a dielectric substrate.
23. The method of any of claims 1 to 21, wherein first a dielectric isolation layer is formed on a conductive substrate, followed by deposition of a current carrying thin film and then an electron emissive thin film.
- 45     24. The method of claim 23, wherein the isolation layer is reactively deposited onto the conductive substrate by chemical vapour deposition or reaction of the surface with a gas or by liquid phase deposition.
25. The method of claim 1, wherein a thin film of an electron emissive material is deposited onto a current carrying bulk semiconductor substrate.
- 50     26. The method of claim 1, wherein a thin film of an electron emissive material is deposited onto a current carrying layer of reduced lead silicate glass overlying a mechanical support of unreduced lead silicate glass.
27. The method of claim 1, wherein first a thin film of current carrying material is deposited onto a dielectric substrate and then the free surface of said current carrying film is altered to exhibit emissive properties by exposing said free surface to a reactive gas.
- 55     28. The method of claim 27, wherein the reactive gas is a material selected from the group consisting of  $\text{NH}_3$  and  $\text{O}_2$ .

29. The method of claim 1, wherein first a thin film of current carrying material is deposited onto a dielectric substrate and then a layer of electron emissive material is deposited by liquid phase deposition (LPD) from a supersaturated solution of such layer-forming material.
- 5    30. The method of claim 29, wherein the emissive material is SiO<sub>2</sub> and the supersaturated solution contains H<sub>2</sub>SiF<sub>6</sub> and SiO<sub>2</sub> in H<sub>2</sub>O.
- 10    31. The method of claim 1, wherein deposition step comprises at least one of thermal-activated LPCVD; plasma-assisted LPCVD; and photochemically-activated LPCVD.
- 15    32. The method of any of claims 1 to 31, wherein at least one thin film has electrical properties which vary with distance from the substrate.
- 20    33. A method according to claim 1, comprising:  
forming a bulk semiconductor substrate having a free surface and a current carrying portion near said free surface capable of carrying a current adequate to replace emitted electrodes and to establish an accelerating field for said emitted electrons and forming a thin-layer on the free surface of the semiconductor having an emissive property by altering the free surface of the substrate by exposing it to a reactive gas, said emissive property having a secondary electron yield capable of resulting in electron multiplication.
- 25    34. A method according to claim 1, comprising the steps of:  
forming a substrate having a free surface and a current carrying portion near said free surface capable of carrying a current adequate to replace emitted electrons to establish an accelerating field for said emitted electrons and forming at least one thin layer at the free surface having an emissive property by liquid phase deposition (LPD), said emissive portion having a secondary electron yield capable of resulting in electron multiplication.
- 30    35. The method of claim 34, wherein the emissive layer is a film of SiO<sub>2</sub> formed from a supersaturated aqueous solution of H<sub>2</sub>SiF<sub>6</sub> and SiO<sub>2</sub> with a small addition of H<sub>3</sub>BO<sub>3</sub>.
- 35    36. The method of claim 34 or 35, wherein LPD occurs at 25-50°C.

#### Patentansprüche

- 35    1. Verfahren zum Ausbilden einer Dynode für einen Kanalelektronenvervielfacher oder eine Mikrokanalplatte, das folgende Schritte umfaßt:
- 40    - Ausbilden eines Substrats (66) zur Schaffung einer Kanaloberfläche; und  
- Ausbilden wenigstens eines dünnen Films auf der Kanaloberfläche, um in irgendeiner Kombination einen stromführenden Abschnitt (64) und einen Elektronenemissionsabschnitt (62) zu erzeugen, dadurch gekennzeichnet, daß:  
- der dünne Film durch Oxidation oder Nitrierung oder durch eine Oberflächenreaktion mit einem Agens erzeugt wird, das durch chemische Gasphasenabscheidung bei reduziertem Druck oder durch Flüssigphasenabscheidung gebildet wird.
- 45    2. Verfahren nach Anspruch 1, wobei der dünne Film durch eine chemische Gasphasenabscheidung (CVD) gebildet wird, welche die Reaktion eines Gases in Anwesenheit eines Substrats bei einer Temperatur und einem Druck umfaßt, die ausgewählt werden, um eine CVD Kinetik zu erzielen, welche durch Grenzflächenprozesse zwischen dem Gas und dem Substrat dominiert wird.
- 50    3. Verfahren nach Anspruch 2, das ferner die Ausbildung mindestens eines Kanals in dem Substrat mit einem großen Seitenverhältnis für die darin abzuscheidende Dynode umfaßt.
- 55    4. Verfahren nach Anspruch 3, das ferner die Ausbildung der Dynode wenigstens um eine ausgewählte Länge gleichmäßig entlang der Kanalwand umfaßt.
5. Verfahren nach einem der Ansprüche 2 bis 4, wobei die Temperatur t = 300°C ≤ T ≤ 1200°C ist.

6. Verfahren nach einem der Ansprüche 2 bis 5, wobei der Druck unter 1300 Pa (10 torr) liegt.
7. Verfahren nach Anspruch 6, wobei der Druck unter 130 Pa (1 torr) liegt.
- 5 8. Verfahren nach Anspruch 7, wobei der Druck zwischen 130 und 13 Pa (1 torr und 0,1 torr) liegt.
9. Verfahren nach einem der Ansprüche 1 bis 8, wobei das Substrat ein Material enthält, das aus der Gruppe bestehend aus  $\text{Si}_3\text{N}_4$ , AlN,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  Glas,  $\text{R}_2\text{O}\text{-}\text{Al}_2\text{O}_3\text{-}\text{SiO}_2$  ( $\text{R} = \text{Li}, \text{Na}, \text{K}$ ) Gläser,  $\text{R}_2\text{O}\text{-}\text{BaO}\text{-}\text{Bi}_2\text{O}_3\text{-Pbo}\text{-}\text{SiO}_2$  ( $\text{R} = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ ) Gläser, AlAs, GaAs, InP, GaP, Si, Si mit einer  $\text{SiO}_2$  Isolationsschicht und GaAs oder InP mit einer  $\text{Si}_3\text{N}_4$  Isolationsschicht ausgewählt wird.
- 10 10. Verfahren nach einem der Ansprüche 1 bis 9, wobei der Elektronvervielfacher eine Mikrokanalplatte ist, und die Substratmaterialien einen Widerstand von  $r \geq 10^8 \Omega\text{-cm}$  aufweisen.
- 15 11. Verfahren nach einem der Ansprüche 1 bis 9, wobei der Elektronvervielfacher ein CEM ist, und das Substrat einen Widerstand  $r$  von  $10^5 \Omega\text{-cm} \leq r \leq 10^5 \Omega\text{-cm}$  aufweist.
12. Verfahren nach einem der Ansprüche 1 bis 9, wobei der Elektronvervielfacher ein CEM oder ein MEM ist, und das Substrat einen Widerstand von  $r \geq 10^{12} \Omega\text{-cm}$  aufweist.
- 20 13. Verfahren nach einem der Ansprüche 1 bis 12, wobei der Emissionsabschnitt einen Dünnfilm enthält aus einem oder mehreren Materialien, die aus der Gruppe bestehend aus  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{SnO}_2$ ,  $\text{BaO}$ ,  $\text{Cs}_2\text{O}$ ,  $\text{Si}_3\text{N}_4$ ,  $\text{Si}_{x}\text{O}_y\text{N}_z$ , C (Diamant) BN und AlN; Emittier mit einer negativen Elektronenaffinität  $\text{GaP:Cs-O}$ ,  $\text{GaP:Ba-O}$ ,  $\text{GaAs:Cs-O}$ ,  $\text{InP:Cs-O}$  und  $\text{Si:Cs-O}$  ausgewählt werden.
- 25 14. Verfahren nach einem der Ansprüche 1 bis 13, wobei der Emissionsabschnitt einen Dünnfilm mit einer Dicke von 2 bis 20 nm enthält.
15. Verfahren nach einem der Ansprüche 1 bis 14, wobei die Ausgangsstoffe für den Emissionsabschnitt Materialien enthalten, welche aus der Gruppe bestehend aus  $\text{SiH}_4$ ,  $\text{SiCl}_x\text{H}_y$ ,  $\text{Si}(\text{OC}_2\text{H}_5)_4$ ,  $\beta$ -Diketonverbindungen von Al (z.B.  $\text{Al}(\text{C}_5\text{HO}_2\text{F}_6)_3$ ),  $\text{Al}(\text{CH}_3)_3$ ,  $\beta$ -Diketonverbindungen von Mg (z.B.  $\text{Mg}(\text{C}_5\text{HO}_2\text{F}_6)_2$ ),  $\text{SnCl}_4$ ,  $\beta$ -Diketonverbindungen von Ba (z.B.  $\text{Ba}(\text{C}_{11}\text{H}_{19}\text{O}_2)_2$ ),  $\text{CH}_4$ , Cs,  $\text{B}_2\text{H}_6$ ,  $\text{Ga}(\text{C}_2\text{H}_5)_3$ ,  $\text{Ga}(\text{CH}_3)_3$ ,  $\text{PH}_3$ ,  $\text{AsH}_3$ ,  $\text{In}(\text{CH}_3)_3$ ,  $\text{O}_2$ ,  $\text{NO}$ ,  $\text{N}_2\text{O}$ ,  $\text{N}_2$  und  $\text{NH}_3$  ausgewählt werden.
- 35 16. Verfahren nach einem der Ansprüche 1 bis 15, wobei die Elektronenemissionsschicht eine erste Grenzenergie, bei welcher  $\delta = 1$ , im Bereich von  $10 \text{ eV} \leq E_p^1 \leq 50 \text{ eV}$  aufweist.
17. Verfahren nach einem der Ansprüche 1 bis 16, wobei der stromführende Abschnitt ein Dünnfilmmaterial enthält, welches aus der Gruppe bestehend aus As-, B- oder P-dotiertem Si, Ge (undotiert), Si (undotiert),  $\text{SiO}_x$ , (SIPOS),  $\text{Si}_x\text{N}_y$ ,  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  und  $\text{SnO}_x$  ausgewählt wird.
- 40 18. Verfahren nach einem der Ansprüche 1 bis 17, wobei der stromführende Abschnitt einen Dünnfilm mit einer Dicke von 10-1000 nm enthält.
- 45 19. Verfahren nach einem der Ansprüche 1 bis 18, wobei Ausgangsstoffe für die Materialien, welche den stromführenden Abschnitt ausbilden, Materialien umfassen, welche aus der Gruppe bestehend aus  $\text{SiH}_4$ ,  $\text{PH}_3$ ,  $\text{GeH}_4$ ,  $\text{B}_2\text{H}_6$ ,  $\text{AsH}_3$ ,  $\text{SnCl}_4$ ,  $\text{Ga}(\text{C}_2\text{H}_5)_3$ ,  $\text{Ga}(\text{CH}_3)_3$ ,  $\text{Al}(\text{CH}_3)_3$ ,  $\text{N}_2\text{O}$ ,  $\text{N}_2$  und  $\text{NH}_3$  ausgewählt werden.
- 50 20. Verfahren nach einem der Ansprüche 1 bis 9 oder 12 bis 19, wobei der stromführende Abschnitt einen Dünnfilm enthält mit einem Flächenwiderstand  $R_s$  von  $10^6 \Omega/\text{sq} \leq R_s \leq 10^8 \Omega/\text{sq}$  für Kanalelektronenvervielfacher und magnetische Elektronenvervielfacher.
21. Verfahren nach einem der Ansprüche 1 bis 8 oder 10 bis 19, wobei der stromführende Abschnitt einen Dünnfilm mit einem Flächenwiderstand  $R_s$  von  $10^{11} \Omega/\text{sq} \leq R_s \leq 10^{14} \Omega/\text{sq}$  für Mikrokanalplatten enthält.
- 55 22. Verfahren nach einem der Ansprüche 1 bis 21, wobei zunächst ein Dünnfilm aus einem stromführenden Material und dann ein Dünnfilm aus einem Elektronenemissionsmaterial auf einem dielektrischen Substrat abgeschieden werden.

23. Verfahren nach einem der Ansprüche 1 bis 21, wobei zunächst eine dielektrische Isolationsschicht auf einem leitenden Substrat ausgebildet und sodann ein stromführender Dünnfilm und hernach ein Elektronenemissionsdünnpfilm abgeschieden wird.
- 5    24. Verfahren nach Anspruch 23, wobei die Isolationsschicht auf dem leitenden Substrat durch chemische Gasphasenabscheidung oder durch Reaktion der Oberfläche mit einem Gas oder durch Flüssigphasenabscheidung reaktionsmäßig abgeschieden wird.
- 10    25. Verfahren nach Anspruch 1, wobei ein Dünnfilm aus Elektronenemissionsmaterial auf einem stromführenden Volumenhalbleitersubstrat abgeschieden wird.
- 15    26. Verfahren nach Anspruch 1, wobei ein Dünnfilm aus Elektronenemissionsmaterial auf einer stromführenden Schicht aus reduziertem Bleisilikatglas abgeschieden wird, welche auf einem mechanischen Träger aus unreduziertem Bleisilikatglas liegt.
- 20    27. Verfahren nach Anspruch 1, wobei zunächst ein Dünnfilm aus stromführendem Material auf einem dielektrischen Substrat abgeschieden wird und sodann die freie Oberfläche des stromführenden Films zur Annahme von Emissionseigenschaften verändert wird, indem die freie Oberfläche einem reaktiven Gas ausgesetzt wird.
- 25    28. Verfahren nach Anspruch 27, wobei das reaktive Gas ein Material ist, welches aus der Gruppe bestehend aus  $\text{NH}_3$  und  $\text{O}_2$  ausgewählt wird.
- 30    29. Verfahren nach Anspruch 1, wobei zunächst ein Dünnfilm aus stromführenden Material auf einem dielektrischen Substrat abgeschieden wird und sodann eine Schicht aus Elektronenemissionsmaterial durch Flüssigphasenabscheidung (LPD) aus einer übersättigten Lösung eines solchen schichtbildenden Materials abgeschieden wird.
- 35    30. Verfahren nach Anspruch 29, wobei das Emissionsmaterial  $\text{SiO}_2$  ist und die übersättigte Lösung  $\text{H}_2\text{SiF}_6$  und  $\text{SiO}_2$  in  $\text{H}_2\text{O}$  enthält.
- 40    31. Verfahren nach Anspruch 1, wobei der Abscheidungsschritt wenigstens einen Schritt einer thermisch-aktivierter LPCVD, einer plasma-unterstützten LPCVD und einer photochemisch-aktivierten LPCVD enthält.
- 45    32. Verfahren nach einem der Ansprüche 1 bis 31, wobei wenigstens ein Dünnfilm elektrische Eigenschaften aufweist, welche sich mit zunehmenden Abstand vom Substrat verändern.
- 50    33. Verfahren nach Anspruch 1, mit:  
Ausbilden eines Volumenhalbleitersubstrats mit einer freien Oberfläche und einem stromführenden Abschnitt in der Nähe der freien Oberfläche, der einen geeigneten Strom führen kann, um emittierte Elektronen zu ersetzen und ein Beschleunigungsfeld für diese emittierten Elektronen zu schaffen, und Ausbilden einer Dünnschicht auf der freien Oberfläche des Halbleiters mit einer Emissionseigenschaft, welche durch Verändern der freien Oberfläche des Substrats erzielt wird, indem dieses einem reaktiven Gas ausgesetzt wird, wobei die Emissionseigenschaft eine Sekundärelektronenausbeute umfaßt, welche eine resultierende Elektronenmultiplikation ermöglicht.
- 55    34. Verfahren nach Anspruch 1, mit den Schritten:  
Ausbilden eines Substrats mit einer freien Oberfläche und einem stromführenden Abschnitt in der Nähe der freien Oberfläche, welche einen geeigneten Strom führen kann, um emittierte Elektronen zu ersetzen und ein Beschleunigungsfeld für diese emittierten Elektronen zu schaffen, und Ausbilden von wenigstens einer Dünnschicht an der freien Oberfläche mit einer Emissionseigenschaft durch Flüssigphasenabscheidung (LPD), wobei die Emissionseigenschaft eine Sekundärelektronenausbeute umfaßt, welche eine resultierende Elektronenmultiplikation ermöglicht.
- 60    35. Verfahren nach Anspruch 34, wobei die Emissionsschicht ein Film aus  $\text{SiO}_2$  ist, die aus einer übersättigten wascherhaltigen Lösung von  $\text{H}_2\text{SiF}_6$  und  $\text{SiO}_2$  mit einem kleinen Zusatz von  $\text{H}_3\text{BO}_3$  gebildet wird.
- 65    36. Verfahren nach Anspruch 34 oder 35, wobei LPD bei 25-50°C stattfindet.

**Revendications**

1. Procédé de formation d'une dynode continue pour un multiplicateur électronique à canal ou une plaque micro-canal, comprenant les étapes de :

5                   formation d'un substrat (66) constituant une surface de canal ; et  
 formation sur la surface de canal d'au moins un film mince afin de produire selon une certaine combinaison une partie de support de courant (64) et une partie d'émission d'électrons (62),

10                  caractérisé en ce que :  
 ledit film mince est produit au moyen d'une oxydation ou d'une nitruration à l'aide d'une réaction de surface avec un agent, ledit agent étant formé par un dépôt chimique en phase vapeur à pression réduite ou par un dépôt en phase liquide.

15                  2. Procédé selon la revendication 1, dans lequel le film mince est formé au moyen d'un dépôt chimique en phase vapeur (CVD) incluant l'étape consistant à faire réagir une vapeur en présence du substrat à une température et à une pression choisies pour aboutir à des vitesses de CVD qui sont dominées par des processus inter-faciaux entre la vapeur et le substrat.

20                  3. Procédé selon la revendication 2, comprenant en outre la formation d'au moins un canal dans le substrat présentant un rapport d'allongement élevé pour le dépôt de la dynode dedans.

4. Procédé selon la revendication 3, comprenant en outre la formation de la dynode de façon conforme sur la paroi de canal le long d'au moins sa longueur choisie.

25                  5. Procédé selon l'une quelconque des revendications 2 à 4, dans lequel la température T est telle que  $300^{\circ}\text{C} \leq T \leq 1200^{\circ}\text{C}$ .

30                  6. Procédé selon l'une quelconque des revendications 2 à 5, dans lequel la pression est inférieure à 1300 Pa (10 Torr).

7. Procédé selon la revendication 6, dans lequel la pression est inférieure à 130 Pa (1 Torr).

8. Procédé selon la revendication 7, dans lequel la pression est comprise entre 130 et 13 Pa (1 Torr et 0,1 Torr).

35                  9. Procédé selon l'une quelconque des revendications 1 à 8, dans lequel le substrat comprend un matériau choisi parmi le groupe comprenant  $\text{Si}_3\text{N}_4$ , AlN,  $\text{Al}_2\text{O}_3$ , verre de  $\text{SiO}_2$ , verres de  $\text{R}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$  ( $\text{R} = \text{Li}, \text{Na}, \text{K}$ ), verres de  $\text{R}_2\text{O}-\text{BaO}-\text{Bi}_2\text{O}_3-\text{PbO}-\text{SiO}_2$  ( $\text{R} = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ ), AlAs, GaAs, InP, GaP, Si, Si avec une couche d'isolation en  $\text{SiO}_2$  et GaAs ou InP avec une couche d'isolation en  $\text{Si}_3\text{N}_4$ .

40                  10. Procédé selon l'une quelconque des revendications 1 à 9, dans lequel le multiplicateur d'électrons est une plaque micro-canal et les matériaux de substrat présentent une résistivité  $R \geq 10^8 \Omega\cdot\text{cm}$ .

11. Procédé selon l'une quelconque des revendications 1 à 9, dans lequel le multiplicateur d'électrons est un CEM et le substrat présente une résistivité  $r$  de  $10^5 \Omega\cdot\text{cm} \leq r \leq 10^8 \Omega\cdot\text{cm}$ .

45                  12. Procédé selon l'une quelconque des revendications 1 à 9, dans lequel le multiplicateur d'électrons est un CEM ou un MEM et le substrat présente une résistivité  $r \geq 10^{12} \Omega\cdot\text{cm}$ .

13. Procédé selon l'une quelconque des revendications 1 à 12, dans lequel la partie d'émission comprend un film mince en un ou plusieurs matériaux choisis parmi le groupe comprenant  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{SnO}$ ,  $\text{BaO}$ ,  $\text{Cs}_2\text{O}$ ,  $\text{Si}_3\text{N}_4$ ,  $\text{Si}_x\text{O}_y\text{N}_z$ , C (diamant), BN et AlN ; et des émetteurs à affinité électronique négative en  $\text{GaP:Cs-O}$ ,  $\text{GaP:Ba-O}$ ,  $\text{GaAs:Cs-O}$ ,  $\text{InP:Cs-O}$  et  $\text{Si:Cs-O}$ .

50                  14. Procédé selon l'une quelconque des revendications 1 à 13, dans lequel la partie d'émission comprend un film mince présentant une épaisseur de 2 à 20 nm.

55                  15. Procédé selon l'une quelconque des revendications 1 à 14, dans lequel des précurseurs pour la partie d'émission incluent des matériaux choisis parmi le groupe comprenant :  $\text{SiH}_4$ ,  $\text{SiCl}_x\text{H}_y$ ,  $\text{Si}(\text{OC}_2\text{H}_5)_4$ , des composés  $\beta$ -dicéto-

nate d'Al (par exemple Al(C<sub>5</sub>HO<sub>2</sub>F<sub>6</sub>)<sub>3</sub>), Al(CH<sub>3</sub>)<sub>3</sub>, des composés  $\beta$ -dicétionate de Mg (par exemple Mg(C<sub>5</sub>HO<sub>2</sub>F<sub>6</sub>)<sub>2</sub>), SnCl<sub>4</sub>, des composés  $\beta$ -dicétionate de Ba (par exemple Ba(C<sub>11</sub>H<sub>19</sub>O<sub>2</sub>)<sub>2</sub>), CH<sub>4</sub>, Cs, B<sub>2</sub>H<sub>6</sub>, Ga(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>, Ga(CH<sub>3</sub>)<sub>3</sub>, PH<sub>3</sub>, AsH<sub>3</sub>, In(CH<sub>3</sub>)<sub>3</sub>, O<sub>2</sub>, NO, N<sub>2</sub>O, N<sub>2</sub> et NH<sub>3</sub>.

- 5      16. Procédé selon l'une quelconque des revendications 1 à 15, dans lequel la partie d'émission d'électrons présente une première énergie \* pour laquelle  $\delta = 1$  dans la plage de 10 eV  $\leq E_p \leq 50$  eV.
- 10     17. Procédé selon l'une quelconque des revendications 1 à 16, dans lequel la partie de support de courant comprend un matériau en film mince choisi parmi le groupe comprenant du Si dopé à l'As, au B ou au P, du Ge (non dopé), du Si (non dopé), du SiO<sub>x</sub> (SIPOS), du Si<sub>x</sub>N<sub>y</sub>, de l'Al<sub>x</sub>Ga<sub>1-x</sub>As et du SnO.
- 15     18. Procédé selon l'une quelconque des revendications 1 à 17, dans lequel la partie de support de courant comprend un film mince présentant une épaisseur de 10 à 1000 nm.
- 20     19. Procédé selon l'une quelconque des revendications 1 à 18, dans lequel des précurseurs pour les matériaux formant la partie de support de courant comprennent des matériaux choisis parmi le groupe comprenant : SiH<sub>4</sub>, PH<sub>3</sub>, GeH<sub>4</sub>, B<sub>2</sub>H<sub>6</sub>, AsH<sub>3</sub>, SnCl<sub>4</sub>, Ga(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>, Ga(CH<sub>3</sub>)<sub>3</sub>, Al(CH<sub>3</sub>)<sub>3</sub>, N<sub>2</sub>O, N<sub>2</sub> et NH<sub>3</sub>.
- 25     20. Procédé selon l'une quelconque des revendications 1 à 9 ou 12 à 19, dans lequel la partie de support de courant comprend un film mince présentant une résistance par carré R<sub>s</sub> de 10<sup>6</sup>  $\Omega$ /carré  $\leq R_s \leq 10^8$   $\Omega$ /carré pour des multiplieurs d'électrons à canal et pour des multiplieurs d'électrons magnétiques.
- 30     21. Procédé selon l'une quelconque des revendications 1 à 8 ou 10 à 19, dans lequel la partie de support de courant comprend un film mince présentant une résistance par carré R<sub>s</sub> de 10<sup>11</sup>  $\Omega$ /carré  $\leq R_s \leq 10^{14}$   $\Omega$ /carré pour des plaques micro-canal.
- 35     22. Procédé selon l'une quelconque des revendications 1 à 21, dans lequel tout d'abord un film mince en un matériau de support de courant puis un film mince en un matériau d'émission d'électrons sont déposés sur un substrat diélectrique.
- 40     23. Procédé selon l'une quelconque des revendications 1 à 21, dans lequel tout d'abord une couche d'isolation diélectrique est formée sur un substrat conducteur, ceci étant suivi par un dépôt d'un film mince de support de courant puis d'un film mince d'émission d'électrons.
- 45     24. Procédé selon la revendication 23, dans lequel la couche d'isolation est déposée de manière réactive sur le substrat conducteur au moyen d'un dépôt chimique en phase vapeur ou d'une réaction de la surface avec un gaz ou au moyen d'un dépôt en phase liquide.
- 50     25. Procédé selon la revendication 1, dans lequel un film mince en un matériau d'émission d'électrons est déposé sur un substrat semi-conducteur dans la masse de support de courant.
- 55     26. Procédé selon la revendication 1, dans lequel un film mince en un matériau d'émission d'électrons est déposé sur une couche de support de courant en verre de silicate de plomb réduit recouvrant un support mécanique en verre de silicate de plomb non réduit.
- 60     27. Procédé selon la revendication 1, dans lequel tout d'abord un film mince en un matériau de support de courant est déposé sur un substrat diélectrique puis la surface libre dudit film de support de courant est altérée de manière à présenter des propriétés d'émission en exposant ladite surface libre à un gaz réactif.
- 65     28. Procédé selon la revendication 27, dans lequel le gaz réactif est un matériau choisi parmi le groupe comprenant NH<sub>3</sub> et O<sub>2</sub>.
- 70     29. Procédé selon la revendication 1, dans lequel tout d'abord un film mince en un matériau de support de courant est déposé sur un substrat diélectrique puis une couche en un matériau d'émission d'électrons est déposée au moyen d'un dépôt en phase liquide (LPD) à partir d'une solution sur-saturée de ce matériau de formation de couche.
- 75     30. Procédé selon la revendication 29, dans lequel le matériau d'émission est du SiO<sub>2</sub> et la solution sur-saturée contient du H<sub>2</sub>SiF<sub>6</sub> et du SiO<sub>2</sub> dans H<sub>2</sub>O.

31. Procédé selon la revendication 1, dans lequel une étape de dépôt comprend au moins un dépôt pris parmi un dépôt chimique en phase vapeur basse pression (LPCVD) activé thermiquement, un LPCVD assisté plasma et un LPCVD activé photochimiquement.
- 5    32. Procédé selon l'une quelconque des revendications 1 à 31, dans lequel au moins un film mince présente des propriétés électriques qui varient en fonction de la distance par rapport au substrat.
- 10    33. Procédé selon la revendication 1, comprenant :  
la formation d'un substrat semi-conducteur dans la masse présentant une surface libre et une partie de support  
de courant à proximité de ladite surface libre pouvant supporter un courant qui convient pour remplacer des électrons émis et pour rétablir un champ d'accélération pour lesdits électrons émis et pour former une couche mince sur la surface libre du semi-conducteur présentant une propriété d'émission en altérant la surface libre du substrat en l'exposant à un gaz réactif, ladite propriété d'émission présentant un rendement d'électrons secondaires pouvant aboutir à une multiplication des électrons.
- 15    34. Procédé selon la revendication 1, comprenant les étapes de :  
formation d'un substrat comportant une surface libre et une partie de support de courant à proximité de ladite surface libre pouvant supporter un courant qui convient pour remplacer des électrons émis afin d'établir un champ d'accélération pour lesdits électrons émis et pour former au moins une couche mince au niveau de la surface libre  
20    présentant une propriété d'émission au moyen d'un dépôt en phase liquide (LPD), ladite partie d'émission présentant un rendement d'électrons secondaires pouvant aboutir à une multiplication des électrons.
- 25    35. Procédé selon la revendication 34, dans lequel la couche d'émission est un film en SiO<sub>2</sub> formé à partir d'une solution aqueuse sur-saturée de H<sub>2</sub>SiF<sub>6</sub> et de SiO<sub>2</sub> avec une faible quantité d'ajout de H<sub>3</sub>BO<sub>3</sub>.
36. Procédé selon la revendication 34 ou 35, dans lequel le procédé LPD est réalisé entre 25 et 50°C.

30

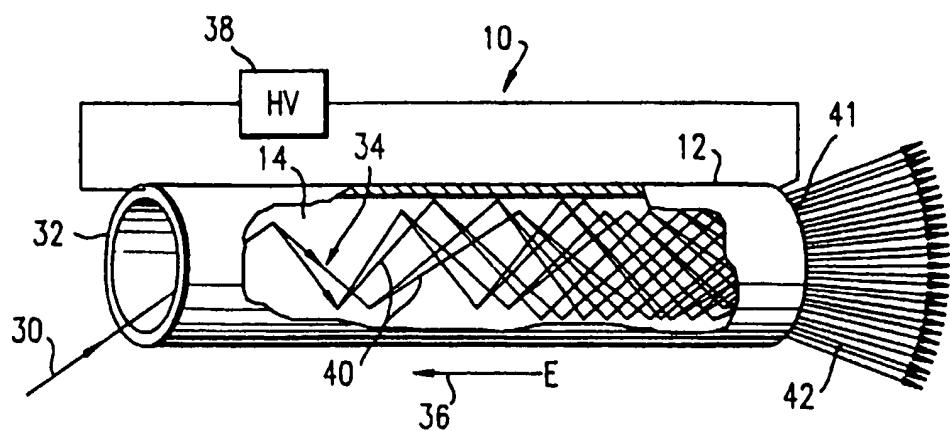
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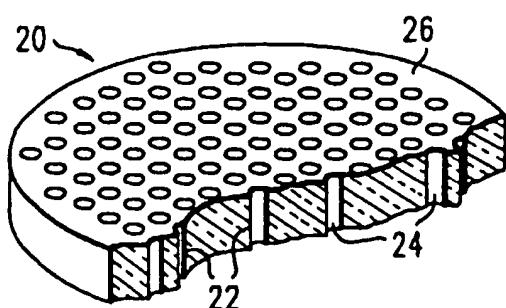
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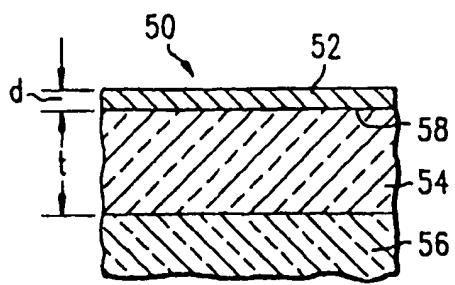
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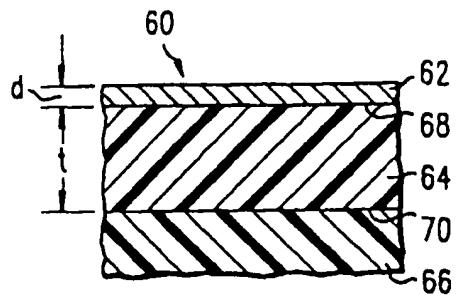
***FIG. 1***



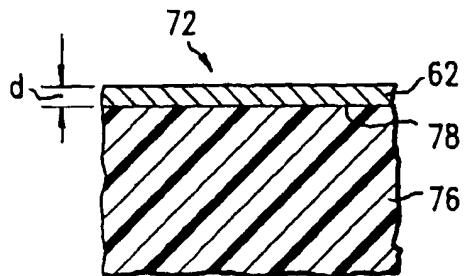
***FIG. 2***



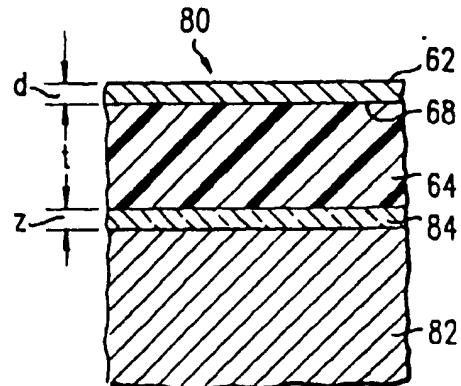
**FIG. 3**



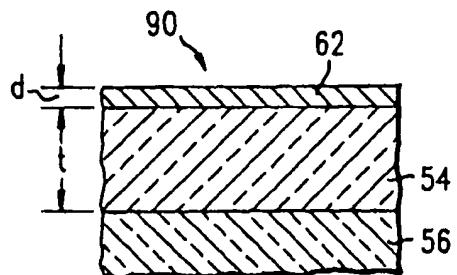
**FIG. 4**



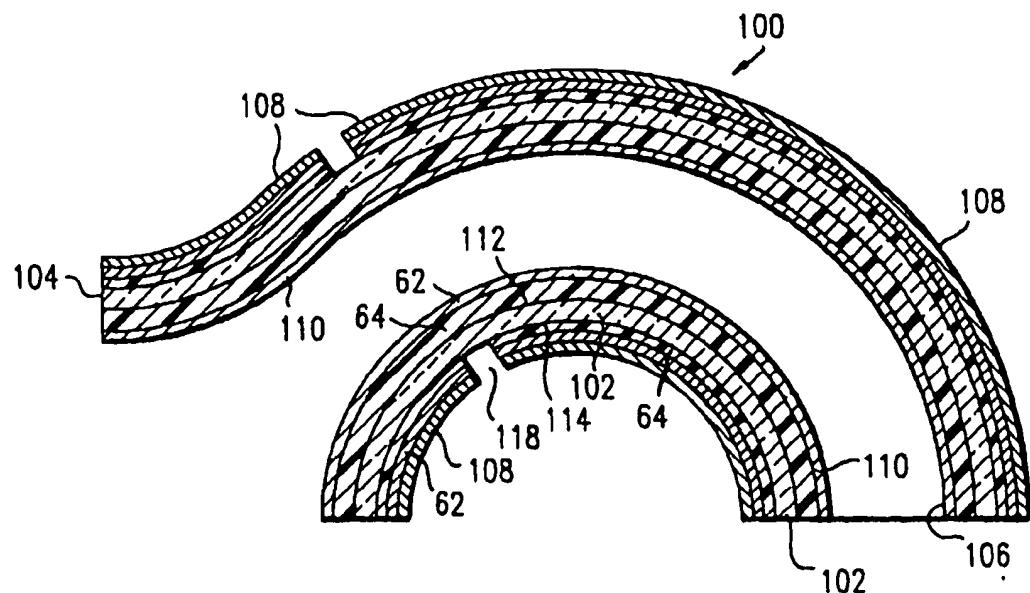
**FIG. 5**



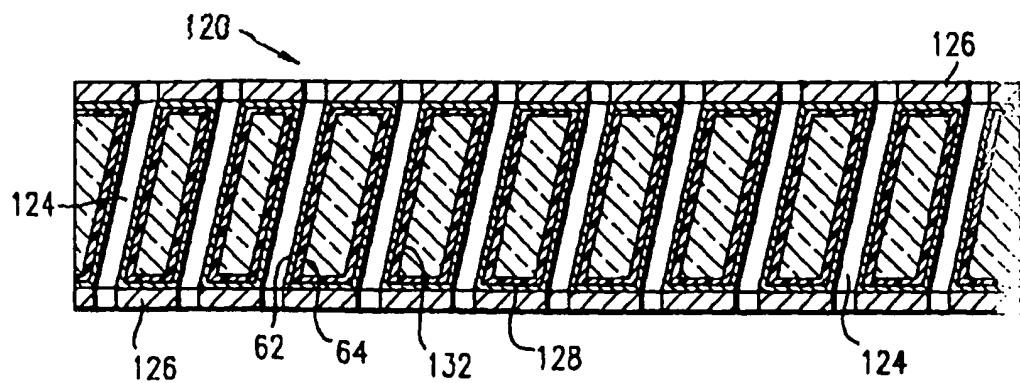
**FIG. 6**



**FIG. 7**



*FIG. 8*



*FIG. 9*

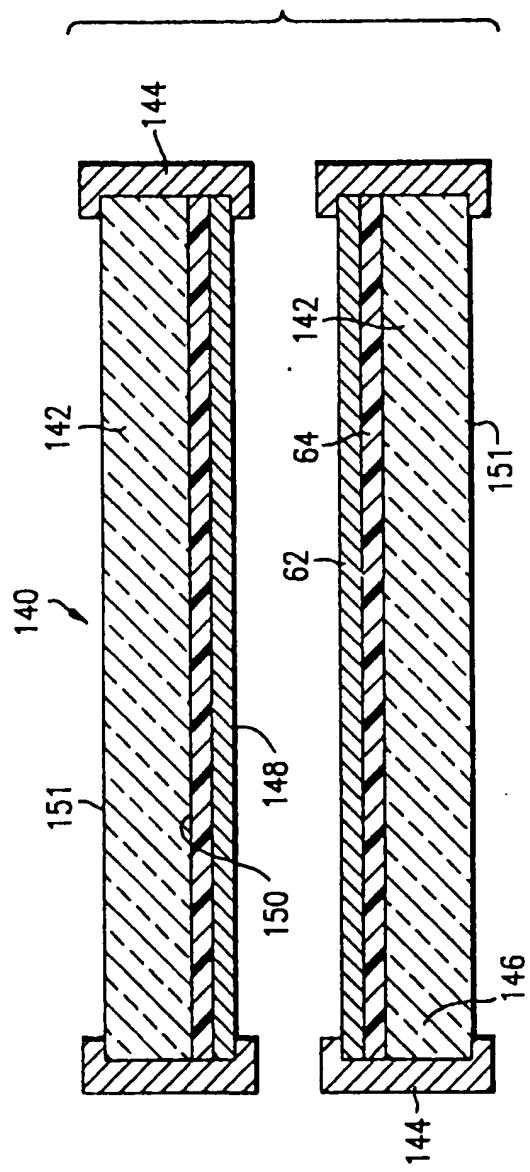
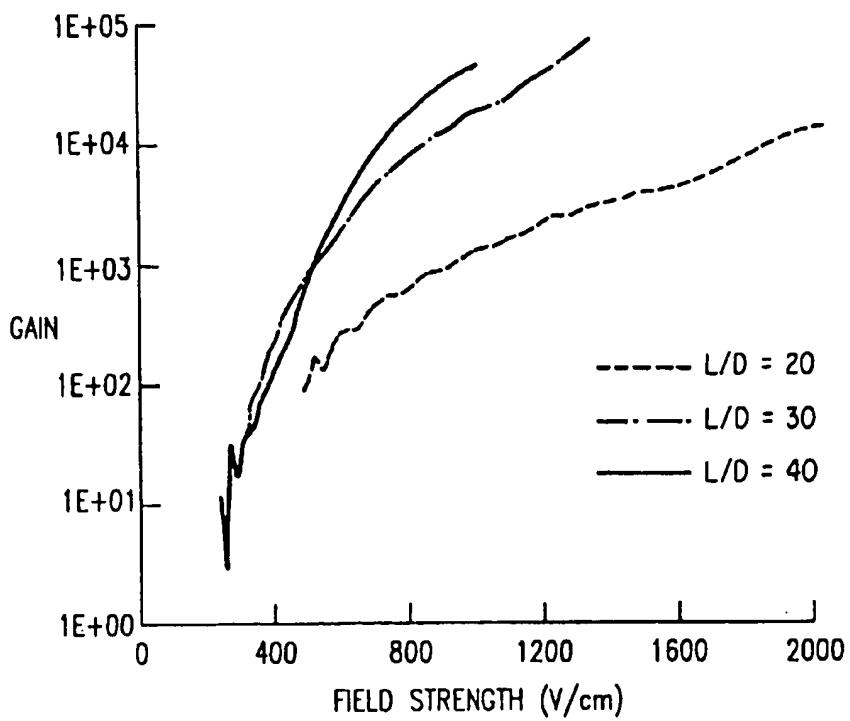
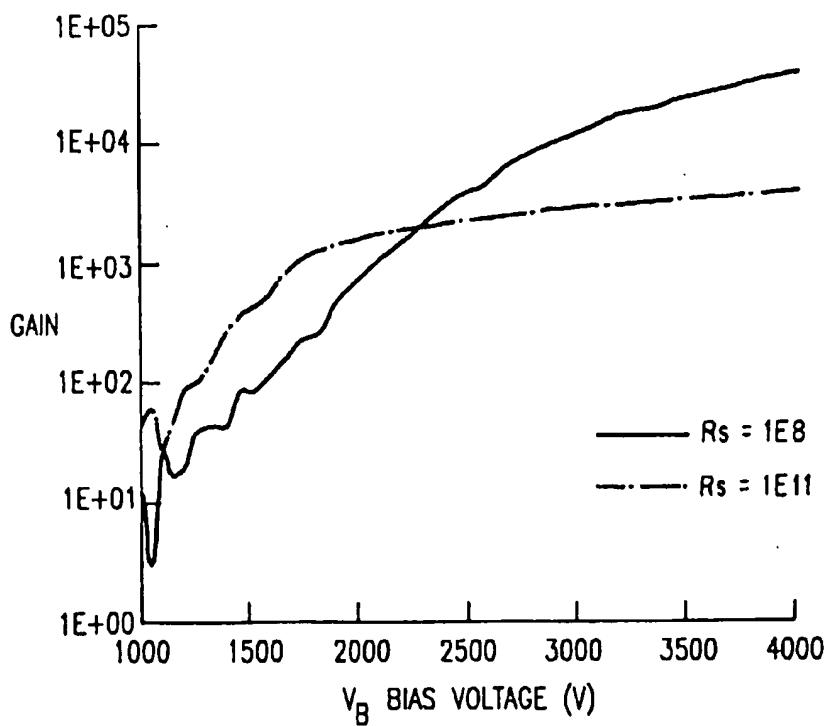
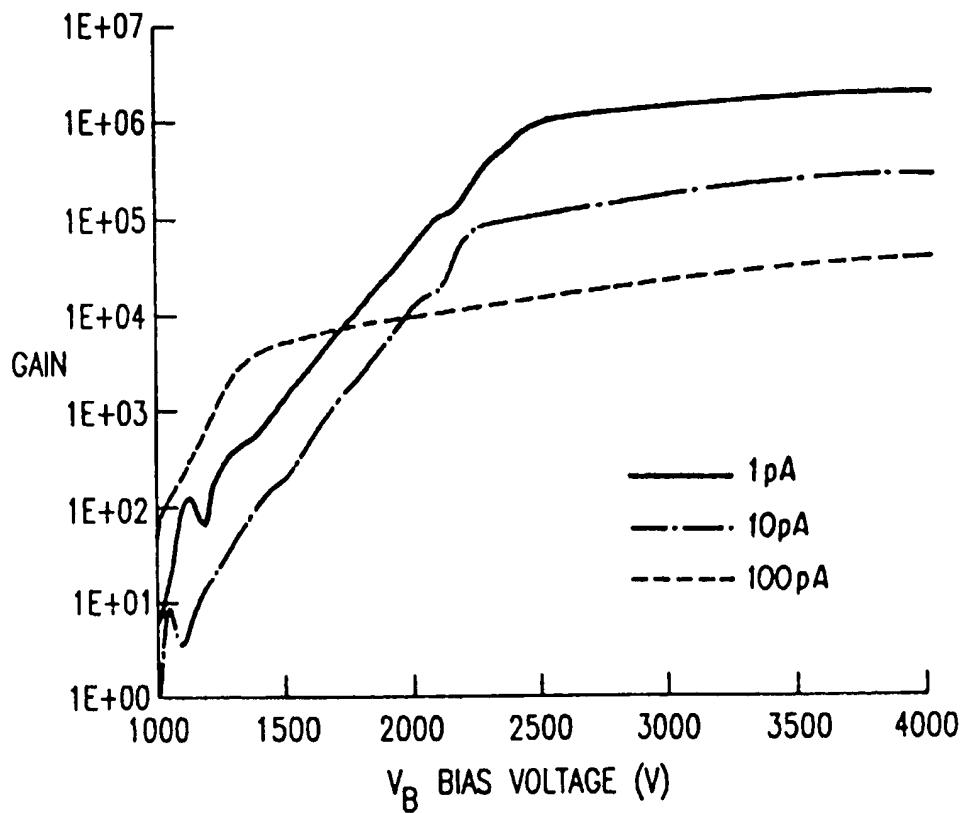


FIG. 10

**FIG. 11****FIG. 12**



**FIG. 13**

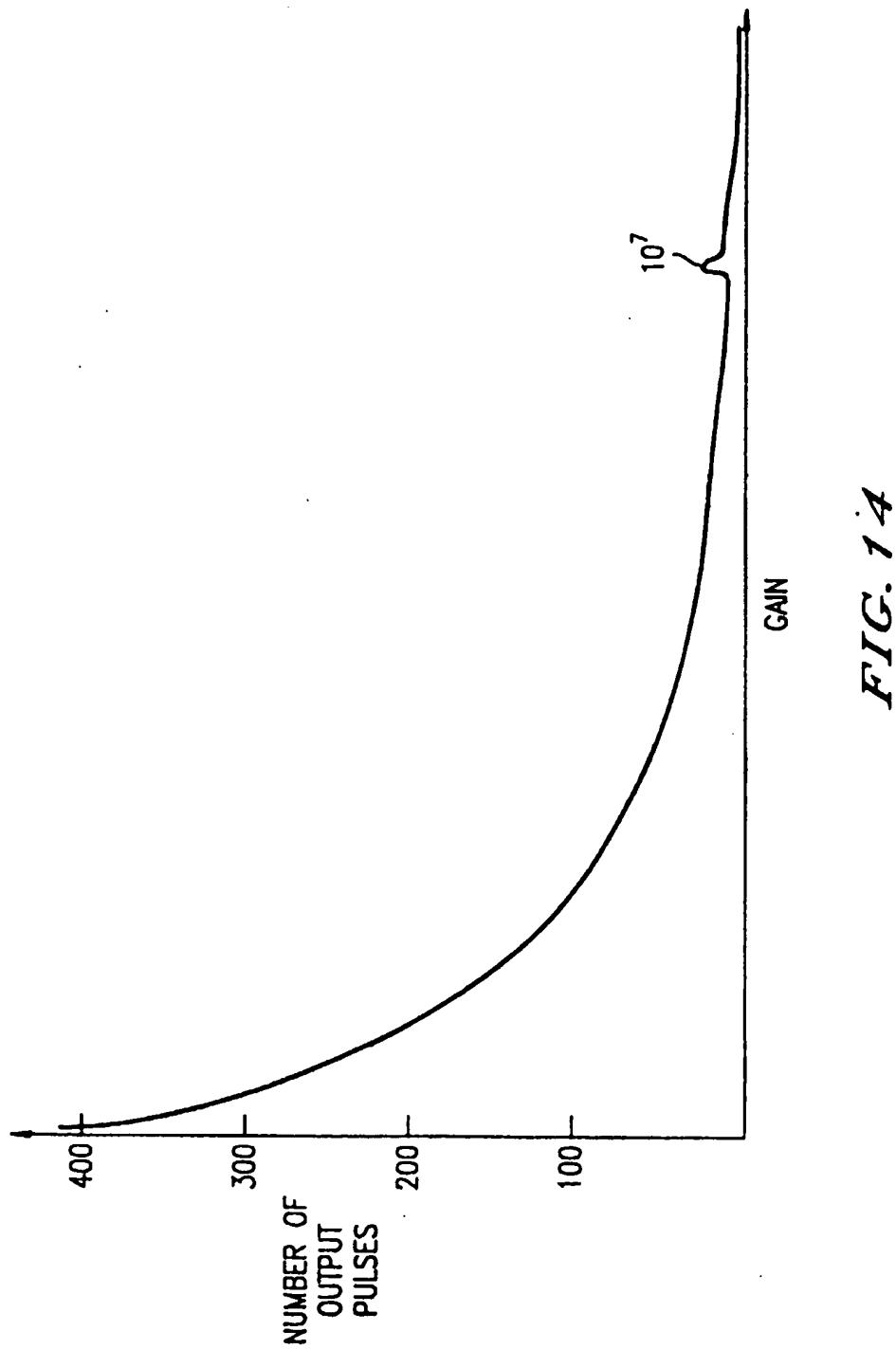


FIG. 14

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